OECD/NEA Nuclear Science Committee
Working Party on Scientific Issues of the Fuel Cycle
Working Group on Lead-bismuth Eutectic

Handbook on Lead-bismuth Eutectic Alloy and Lead Properties, Materials Compatibility, Thermal-hydraulics and Technologies

2007 Edition

© OECD 2007
NEA No. 6195

NUCLEAR ENERGY AGENCY
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

The OECD is a unique forum where the governments of 30 democracies work together to address the economic, social and environmental challenges of globalisation. The OECD is also at the forefront of efforts to understand and to help governments respond to new developments and concerns, such as corporate governance, the information economy and the challenges of an ageing population. The Organisation provides a setting where governments can compare policy experiences, seek answers to common problems, identify good practice and work to co-ordinate domestic and international policies.

The OECD member countries are: Australia, Austria, Belgium, Canada, the Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Japan, Korea, Luxembourg, Mexico, the Netherlands, New Zealand, Norway, Poland, Portugal, the Slovak Republic, Spain, Sweden, Switzerland, Turkey, the United Kingdom and the United States. The Commission of the European Communities takes part in the work of the OECD.

OECD Publishing disseminates widely the results of the Organisation’s statistics gathering and research on economic, social and environmental issues, as well as the conventions, guidelines and standards agreed by its members.

This work is published on the responsibility of the Secretary-General of the OECD. The opinions expressed and arguments employed herein do not necessarily reflect the official views of the Organisation or of the governments of its member countries.

NUCLEAR ENERGY AGENCY

The OECD Nuclear Energy Agency (NEA) was established on 1st February 1958 under the name of the OEEC European Nuclear Energy Agency. It received its present designation on 20th April 1972, when Japan became its first non-European full member. NEA membership today consists of 28 OECD member countries: Australia, Austria, Belgium, Canada, the Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Japan, Luxembourg, Mexico, the Netherlands, Norway, Portugal, Republic of Korea, the Slovak Republic, Spain, Sweden, Switzerland, Turkey, the United Kingdom and the United States. The Commission of the European Communities also takes part in the work of the Agency.

The mission of the NEA is:

- to assist its member countries in maintaining and further developing, through international co-operation, the scientific, technological and legal bases required for a safe, environmentally friendly and economical use of nuclear energy for peaceful purposes, as well as
- to provide authoritative assessments and to forge common understandings on key issues, as input to government decisions on nuclear energy policy and to broader OECD policy analyses in areas such as energy and sustainable development.

Specific areas of competence of the NEA include safety and regulation of nuclear activities, radioactive waste management, radiological protection, nuclear science, economic and technical analyses of the nuclear fuel cycle, nuclear law and liability, and public information. The NEA Data Bank provides nuclear data and computer program services for participating countries.

In these and related tasks, the NEA works in close collaboration with the International Atomic Energy Agency in Vienna, with which it has a Co-operation Agreement, as well as with other international organisations in the nuclear field.

© OECD 2007

No reproduction, copy, transmission or translation of this publication may be made without written permission. Applications should be sent to OECD Publishing: rights@oecd.org or by fax (+33-1) 45 24 99 30. Permission to photocopy a portion of this work should be addressed to the Centre Français d’exploitation du droit de Copie (CFC), 20 rue des Grands-Augustins, 75006 Paris, France, fax (+33-1) 46 34 67 19. (contact@cfcopies.com) or (for US only) to Copyright Clearance Center (CCC), 222 Rosewood Drive Danvers, MA 01923, USA, fax +1 978 646 8600, info@copyright.com.
FOREWORD

Under the auspices of the NEA Nuclear Science Committee (NSC), the Working Party on Scientific Issues of the Fuel Cycle (WPFC) was established to co-ordinate scientific activities regarding various existing and advanced nuclear fuel cycles, including advanced reactor systems, associated chemistry and flow sheets, development and performance of fuels and materials, and accelerators and spallation targets. The WPFC has different subgroups to cover the wide range of scientific fields in the nuclear fuel cycle.

Created in 2002, the Working Group on Lead-bismuth Eutectic (WG-LBE) technology is a WPFC subsidiary group which co-ordinates and guides LBE research in participating organisations while enhancing closer and broader-based collaboration. The aim is to develop a set of requirements and standards as well as consistent methodology for experimentation, data collection and data analyses. It was agreed to publish the results in the form of a handbook. Due to a rising interest in the Pb-cooled option in the Generation IV International Forum, the WG-LBE also decided to include data and technology aspects of both LBE and Pb.

The current edition of the handbook is a state-of-the-art, critical review of existing data and discrepancies, open points and perspectives for both Pb and LBE technological development. The reader may wish to note that the publication of a revised edition of the handbook is foreseen towards 2009 in order to integrate more experimental results from the various national and international research programmes currently being carried out on heavy liquid metal technology.

Acknowledgements

The NEA Secretariat expresses its sincere gratitude to C. Fazio (FZK, Germany), Chair of the working group, for her devotion and excellent leadership, and to the chapter authors and contributors who devoted their time and effort to this handbook preparation. Special thanks are conveyed to the peer reviewers: H.U. Borgstedt (FZK, Germany), C. Latgé (CEA, France), R. Ballinger (MIT, USA) and H. Katsuta (JAEA, Japan), whose work was essential for improving the quality of the handbook. K. Pasamehmetoglu (INL, USA) and J.U. Knebel (FZK, Germany) are thanked for the initiation of this work.
TABLE OF CONTENTS

Foreword ............................................................................................................................................ 3

Chapter 1  INTRODUCTION ............................................................................................................ 15

Chapter 2  THERMOPHYSICAL AND ELECTRIC PROPERTIES ............................................... 25

  2.1 Introduction.................................................................................................................................. 25
  2.2 Pb-Bi alloy phase diagram ........................................................................................................... 26
  2.3 Normal melting point ................................................................................................................... 29
      2.3.1 Lead ....................................................................................................................................... 29
      2.3.2 Bismuth ............................................................................................................................... 29
      2.3.3 LBE ...................................................................................................................................... 31
  2.4 Volume change at melting and solidification .............................................................................. 32
  2.5 Latent heat of melting at the normal melting point ..................................................................... 35
      2.5.1 Lead ....................................................................................................................................... 35
      2.5.2 Bismuth ............................................................................................................................... 36
      2.5.3 LBE ...................................................................................................................................... 36
  2.6 Normal boiling point ................................................................................................................... 37
      2.6.1 Lead ....................................................................................................................................... 37
      2.6.2 Bismuth ............................................................................................................................... 37
      2.6.3 LBE ...................................................................................................................................... 37
  2.7 Heat of vaporisation at the normal boiling point ........................................................................ 39
      2.7.1 Lead ....................................................................................................................................... 39
      2.7.2 Bismuth ............................................................................................................................... 39
      2.7.3 LBE ...................................................................................................................................... 41
  2.8 Saturation vapour pressure .......................................................................................................... 41
      2.8.1 Lead ....................................................................................................................................... 42
      2.8.2 Bismuth ............................................................................................................................... 42
      2.8.3 LBE ...................................................................................................................................... 44
  2.9 Surface tension ........................................................................................................................... 47
      2.9.1 Lead ....................................................................................................................................... 47
      2.9.2 Bismuth ............................................................................................................................... 48
      2.9.3 LBE ...................................................................................................................................... 49
  2.10 Density .......................................................................................................................................... 52
       2.10.1 Lead .................................................................................................................................... 52
       2.10.2 Bismuth ............................................................................................................................. 54
       2.10.3 LBE ................................................................................................................................... 56
  2.11 Thermal expansion .................................................................................................................... 58
  2.12 Sound velocity and compressibility ......................................................................................... 59
       2.12.1 Lead .................................................................................................................................... 60
       2.12.2 Bismuth ............................................................................................................................. 60
       2.12.3 LBE ................................................................................................................................... 62
Chapter 3  THERMODYNAMIC RELATIONSHIPS AND HEAVY LIQUID METAL INTERACTION WITH OTHER COOLANTS

3.1 Introduction........................................................................................................ 101
3.2 Enthalpies, entropies (solid and liquid state) – free energy and entropy of mixing......................................................................................................................... 101
3.3 Purity requirements.................................................................................................. 104
3.4 Solubility data of metallic and non-metallic impurities in LBE and Pb............. 105
   3.4.1 Solubility data of some metallic elements in pure Pb and liquid eutectic Pb-Bi.................................................. 105
   3.4.2 Solubility data of oxygen in pure Pb and LBE............................................. 108
3.5 Diffusivity............................................................................................................... 110
   3.5.1 Diffusivity data of some metallic elements................................................ 110
   3.5.2 Oxygen diffusion coefficient...................................................................... 113
3.6 Chemical interactions and ternary phase diagrams............................................ 114
3.7 Lead and LBE-water interaction.......................................................................... 116
   3.7.1 Literature survey ..................................................................................... 116
   3.7.2 Related risks............................................................................................ 118
   3.7.3 Numerical codes ..................................................................................... 118
3.8 Lead or LBE and sodium interaction.................................................................. 119
3.9 LBE and Pb and organic compounds interaction.............................................. 122

Chapter 4  CHEMISTRY CONTROL AND MONITORING SYSTEMS

4.1 Introduction........................................................................................................ 129
4.2 Oxygen control in lead and LBE systems......................................................... 130
   4.2.1 Upper limit for the oxygen for operational control................................. 130
   4.2.2 Lower limit for the oxygen for operational control.................................. 131
   4.2.3 Specifications for active oxygen control.................................................. 135
   4.2.4 Policy for a nuclear system...................................................................... 137
4.2.5 Oxygen control system ................................................................. 139
4.2.6 The oxygen homogeneity issue .................................................. 141
4.3 Characterisation of impurities and requirements for control ............. 143
  4.3.1 Impurity sources ..................................................................... 143
  4.3.2 Behaviour of impurities and requirements for purification ........... 145
  4.3.3 Active impurities .................................................................... 148
  4.3.4 Production rates assessment .................................................... 148
  4.3.5 Consequences on operations ................................................... 150
4.4 Instruments for chemical monitoring .............................................. 151
  4.4.1 On-line electrochemical oxygen sensor ..................................... 151
    4.4.1.1 Principle ........................................................................... 153
    4.4.1.2 Theory ............................................................................ 155
    4.4.1.3 Calibration ....................................................................... 160
    4.4.1.4 Characteristics of the oxygen sensors ................................ 162
    4.4.1.5 Conclusions ................................................................... 164
  4.4.2 Development of sampling systems and analytical methods ............. 165
    4.4.2.1 Dip sampler validation ..................................................... 165
    4.4.2.2 Chemical analysis of lead-bismuth eutectic ....................... 167
    4.4.2.3 Radioactive nuclides chemical analysis............................. 169
    4.4.2.4 Conclusions ................................................................... 170
4.5 Conclusions ......................................................................................... 170

Chapter 5

PROPERTIES OF IRRADIATED LBE AND Pb ............................................. 179
5.1 Introduction ....................................................................................... 179
5.2 Theoretical considerations ............................................................. 180
  5.2.1 Evaporation characteristics of polonium .................................... 180
  5.2.2 Volatilisation pathways of polonium ......................................... 182
  5.2.3 Evaluation of thermochemical data for binary polonium containing
      systems by means of the semi-empirical Miedema model ............... 188
  5.2.4 Analysis of thermochemical relations of iodine within a liquid
      LBE spallation target ................................................................. 191
5.3 Investigations on irradiated LBE ..................................................... 206
  5.3.1 Release of volatile radionuclides .............................................. 206
    5.3.1.1 Polonium vaporisation ...................................................... 207
    5.3.1.2 Evaporation characteristics of polonium and its lighter
          homologues selenium and tellurium from liquid Pb-Bi
          eutecticum ............................................................................ 210
  5.3.2 Thermal release behaviour of mercury and thallium from liquid
      eutectic lead-bismuth alloy ......................................................... 212
  5.3.3 Release of volatile radionuclides in abnormal operating conditions .... 214
5.4 Irradiation effects ................................................................. 216
  5.4.1 Measurement of gas and volatile element production rates in a
      proton-irradiated molten lead-bismuth target in the ISOLDE facility .... 216
    5.4.1.1 ISOLDE facility and proton beam .................................. 216
    5.4.1.2 ISOLDE target ............................................................... 217
    5.4.1.3 Measurement techniques ............................................... 217
    5.4.1.4 Data analysis .................................................................. 218
    5.4.1.5 First results .................................................................... 221
    5.4.1.6 Conclusions and outlook ............................................... 224
5.4.2 Irradiation experiments.............................................................................. 224
  5.4.2.1 Pb and LBE irradiated in the STIP experiments using
         the Swiss Spallation Neutron Source (SINQ)........................................ 224
  5.4.2.2 LBE irradiated in the LiSoR experiment........................................... 225

Chapter 6
COMPATIBILITY OF STRUCTURAL MATERIALS
WITH LBE AND Pb: STANDARDISATION OF DATA,
CORROSION MECHANISM AND RATE............................................................ 231

  6.1 Introduction ......................................................................................................... 231
  6.2 Fundamentals....................................................................................................... 231
       6.2.1 Corrosion........................................................... 231
       6.2.2 Oxidation........................................................... 233
  6.3 Summary and critical review of the data ............................................................. 238
  6.4 Conclusions and further data needed................................................................. 245
  6.5 Recommendations on corrosion tests procedure (standardisation).................. 245
       6.5.1 Pre-test preparation.................................................................................... 246
           6.5.1.1 Liquid metal: LBE and Pb.................................................... 246
           6.5.1.2 Material ........................................................................ 246
       6.5.2 Test conditions .......................................................................................... 246
           6.5.2.1 Static (no flow) tests............................................................. 246
           6.5.2.2 Dynamic tests ....................................................................... 247
  6.5.3 Post-test analysis .......................................................................................... 248

Chapter 7
EFFECT OF LBE AND LEAD ON MECHANICAL PROPERTIES
OF STRUCTURAL MATERIALS.......................................................................... 275

  7.1 Introduction ......................................................................................................... 275
  7.2 Liquid metal embrittlement ................................................................................. 277
       7.2.1 Wetting: From ideal to real metallic systems............................................ 277
       7.2.2 Definition and criteria of occurrence of LME........................................... 281
  7.3 Environment-assisted cracking............................................................................ 284
       7.3.1 Definition of EAC ..................................................................................... 284
       7.3.2 Phenomenological criteria of occurrence of EAC..................................... 284
  7.4 Tensile behaviour of austenitic and ferritic/martensitic steels in contact
      with lead, LBE and other liquid metals ............................................................... 285
       7.4.1 Definitions................................................................................................. 285
       7.4.2 Tensile behaviour of smooth, rough and notched martensitic
           steel specimens in HLMs .......................................................................... 285
           7.4.2.1 Tensile behaviour of smooth and rough T91 steel
                   specimens in lead, LBE and tin .................................................. 285
           7.4.2.2 Tensile behaviour of T91 steel specimens in LBE,
                   in the presence of flaws ............................................................. 286
           7.4.2.3 Tensile behaviour of MANET II and T91 steels after
                   pre-exposure to LBE...................................................................... 286
           7.4.2.4 Tensile behaviour of T91 in air, at room temperature
                   after pre-exposure to LBE ............................................................. 286
           7.4.2.5 Tensile behaviour of T91 in conditions of direct contact
                   with Pb-Bi.................................................................................. 287
           7.4.2.6 Tensile behaviour and embrittlement of martensitic
                   steels in contact with Li and Pb-17Li ......................................... 287
7.4.3 Experimental results that may be interpreted as LME effects:
Case of T91 in contact with LBE or lead ............................................................ 287
  7.4.3.1 Role of the bulk metallurgical state ................................................... 288
  7.4.3.2 Role of wetting .................................................................................. 289
  7.4.3.3 Role of surface flaws ........................................................................ 292
  7.4.3.4 Role of traces of impurities .............................................................. 294
7.4.4 Main requirements to prevent LME effects .................................................. 294
7.4.5 Experimental results that may be interpreted as EAC effects ..................... 295
  7.4.5.1 Case of some ferritic/martensitic steels in contact with Li and Pb-17Li .......... 295
  7.4.5.2 Case of T91 steel in contact with LBE .............................................. 296
7.5 Fatigue behaviour of austenitic steel of type 316 and ferritic/martensitic steel of type T91 in contact with lead and LBE ................................................................. 296
  7.5.1 Definition ............................................................................................... 296
  7.5.2 Low-cycle fatigue behaviour of ferritic/martensitic steels in contact with LBE ................................................................. 299
    7.5.2.1 Role of LBE on cyclic accommodation ......................................... 299
    7.5.2.2 Role of LBE on fatigue resistance .................................................. 300
  7.5.3 Influence of hold time on fatigue behaviour of T91 in LBE ...................... 301
  7.5.4 Influence of preliminary exposure to LBE on fatigue behaviour of T91 ......... 301
  7.5.5 Influence of LBE on fatigue crack growth of T91 and MANET II ............. 302
  7.5.6 Influence of LBE on fatigue fracture surface morphology of T91 .............. 303
  7.5.7 Influence of LBE on fatigue crack initiation in T91 and MANET II........... 305
  7.5.8 Low-cycle fatigue behaviour of 316L type stainless steel in contact with lead alloys, in comparison with lithium and sodium .................................................. 307
7.6 Creep properties: Definition and state of the art concerning the austenitic steel of type 316 and the ferritic/martensitic steel of type T91 in contact with lead and LBE ................................................................. 308
  7.6.1 Definition ............................................................................................... 308
  7.6.2 Creep properties of martensitic and austenitic stainless steels in air or liquid metals other than lead or LBE ........................................................................ 308
  7.6.3 Creep and creep crack growth of both austenitic and ferritic/ martensitic steels in lead or LBE ................................................................. 309
    7.6.4 Liquid metal accelerated creep (LMAC) ........................................... 309
    7.6.5 Accelerated plastic strain of T91 steel in contact with lead ................. 309
    7.6.6 Creep crack growth on T91 and 316L in contact with LBE or lead ...... 310
7.7 Fracture mechanics: Case of both austenitic steel of type 316 and ferritic/ martensitic steel of type T91 in contact with lead and LBE ................................................................. 310
  7.8 Recommendations for testing procedures .................................................... 311
    7.8.1 ASTM standards useful for mechanical tests in LBE ......................... 311
    7.8.2 Adaptation of experimental installations for HLMs ............................. 313
    7.8.3 Recommendations for testing procedures .......................................... 314
  7.9 Conclusions ............................................................................................... 315

Chapter 7 Annex .......................................................................................................................... 329

Chapter 8 IRRADIATION EFFECTS ON COMPATIBILITY OF STRUCTURAL MATERIALS WITH LEAD-BISMUTH EUTECTIC (LBE) ................................................................. 359
  8.1 Introduction ...
Chapter 9  Pb AND LBE CORROSION PROTECTION AT ELEVATED TEMPERATURES .............................................................. 379
  9.1 Introduction .................................................................................................................................................. 379
  9.2 Methods of surface protection .................................................................................................................. 380
    9.2.1 Alloying of stable oxide formers ....................................................................................................... 380
      9.2.1.1 Alloying by the GESA process .................................................................................................. 381
      9.2.1.2 Diffusion alloying processes ..................................................................................................... 382
    9.2.2 Corrosion-resistant coatings .............................................................................................................. 384
      9.2.2.1 FeCrAlY coatings ....................................................................................................................... 384
      9.2.2.2 Coatings with resistant metals ................................................................................................. 385
      9.2.2.3 Oxide, carbide and nitride coatings .......................................................................................... 386
    9.2.3 Corrosion inhibitors in LBE ................................................................................................................. 386
  9.3 Corrosion examinations on alloys and coatings .......................................................................................... 387
    9.3.1 Surface alloys ..................................................................................................................................... 387
    9.3.2 Bulk alloys ........................................................................................................................................... 387
    9.3.3 Coatings .............................................................................................................................................. 388
  9.4 Concluding remarks .................................................................................................................................. 389

Chapter 10  LOW PRANDTL NUMBER THERMAL-HYDRAULICS .............................................................. 399
  10.1 Introduction ............................................................................................................................................. 399
  10.2 Specific features of liquid metals ............................................................................................................ 400
  10.3 The conservation equations .................................................................................................................... 403
  10.4 Laminar momentum exchange .............................................................................................................. 406
    10.4.1 Channel or tube flow ......................................................................................................................... 406
    10.4.2 Boundary layer equations ................................................................................................................. 408
    10.4.3 Summary and comments .................................................................................................................. 410
  10.5 Laminar energy exchange ....................................................................................................................... 411
    10.5.1 Types of laminar duct flow .............................................................................................................. 412
10.5.2 Fluid flow and heat transfer parameters ............................................... 413
10.5.3 Thermal boundary conditions ................................................................. 415
10.5.4 Laminar heat transfer in circular ducts .................................................... 416
  10.5.4.1 Fully developed flow ........................................................................ 416
  10.5.4.2 Hydrodynamically developing flow .................................................... 418
  10.5.4.3 Thermally developing flow ............................................................... 418
  10.5.4.4 Simultaneously developing flow ....................................................... 420
10.5.5 Summary on the laminar heat transfer .................................................... 422
10.6 Turbulent momentum exchange .................................................................. 423
  10.6.1 Description of turbulence ..................................................................... 424
  10.6.2 Reynolds equations for turbulent flows and derivation
       of transport equations .............................................................................. 425
  10.6.3 A flashlight on turbulence modelling .................................................... 427
  10.6.4 Boundary layer approximations ............................................................ 428
  10.6.5 Summary .............................................................................................. 430
10.7 Turbulent energy exchange .......................................................................... 430
  10.7.1 Reynolds equations for the turbulent energy exchange ......................... 431
  10.7.2 Analogies between fluid flow and heat transfer parameters .................... 431
  10.7.3 Experimental observations of the turbulent heat transport ..................... 434
  10.7.4 Closure methods for the turbulent heat flux .......................................... 436
  10.7.5 Heat transfer correlations for engineering applications ....................... 444
      10.7.5.1 Free convection distortion in liquid metal heat transfer .................. 444
      10.7.5.2 Turbulent heat transfer in circular ducts ..................................... 446
      10.7.5.3 Turbulent heat transfer in a flat duct .......................................... 453
      10.7.5.4 Turbulent heat transfer in a rectangular duct ............................... 455
      10.7.5.5 Turbulent heat transfer in a concentric annulus ............................ 456
      10.7.5.6 Turbulent heat transfer over rod bundles ..................................... 458
10.8 Some final remarks .................................................................................... 461

Chapter 11  INSTRUMENTATION ........................................................................... 479
11.1 Background of the measurement technique development ........................ 479
11.2 Flow meters ............................................................................................... 480
  11.2.1 Electromagnetic flow meters ................................................................. 480
      11.2.1.1 DC electromagnetic flow meters .............................................. 480
      11.2.1.2 AC electromagnetic flow meter (EMFM) ................................. 484
  11.2.2 Momentum-based flow meters ............................................................... 488
      11.2.2.1 Turbine flow meter ................................................................... 488
      11.2.2.2 Gyrostatic flow meters ............................................................. 490
  11.2.3 Pressure- and counter-based flow meters ............................................ 491
      11.2.3.1 Von Karman vortex street flow meter ....................................... 491
      11.2.3.2 Obstacle flow meters, nozzle and orifice flow meters ............... 492
  11.2.4 Ultrasound transit time method (UTT) .................................................. 495
11.3 Pressure sensors .......................................................................................... 498
  11.3.1 Types of pressure gauges and operation experience ............................. 498
  11.3.2 Pressure correction in fully developed turbulent pipe flow ................. 500
11.4 Local velocity measurements .................................................................... 501
  11.4.1 Ultrasound Doppler velocimetry ......................................................... 502
  11.4.2 Permanent magnetic probes (PMP) ...................................................... 505
  11.4.3 Reaction probes (RP) .......................................................................... 507
  11.4.4 Hot wire anemometry (HWA) ............................................................... 509
11.4.5 Transition time methods ........................................................................ 511
  11.4.5.1 Temperature pulse method............................................................ 511
  11.4.5.2 Tracer studies ............................................................................. 512
  11.4.5.3 Dissolution studies .................................................................... 513
11.4.6 Neutron radiography .......................................................................... 514
11.4.7 Fibre mechanics systems (FMS) ......................................................... 514
11.4.8 Pitot and Prandtl tubes ...................................................................... 516
  11.4.8.1 General features and applications .............................................. 516
  11.4.8.2 Viscous corrections for Pitot tubes ............................................. 518
  11.4.8.3 Turbulence correction for Pitot tubes ....................................... 518
  11.4.8.4 Velocity gradient correction for Pitot tubes ............................... 519
  11.4.8.5 Displacement correction for Pitot tubes ..................................... 520
  11.4.8.6 Wall correction of Pitot tubes .................................................... 520
  11.4.8.7 Comments on displacement and corrections.............................. 521
11.5 Void fraction sensors ............................................................................ 521
  11.5.1 Electromagnetic sensors .................................................................. 521
    11.5.1.1 DC permanent magnet void fraction sensors (PMVS) ............. 522
    11.5.1.2 AC electromagnetic void fraction sensors (EMVS) ................. 523
  11.5.2 X-ray, γ-ray and neutron radiography (NR) ..................................... 524
    11.5.2.1 X-ray absorption .................................................................... 525
    11.5.2.2 γ-ray absorption .................................................................... 530
    11.5.2.3 Neutron radiography (NR) ..................................................... 532
  11.5.3 Resistive or conductance probes ...................................................... 536
11.6 Temperature measurements .................................................................. 544
  11.6.1 Thermocouples ............................................................................. 544
  11.6.2 Heat-emitting temperature-sensing surfaces (HETSS) ..................... 550
11.7 Level meters ......................................................................................... 552
  11.7.1 Direct contact sensors .................................................................... 552
  11.7.2 Non-intrusive level sensors .............................................................. 554
    11.7.2.1 Electromagnetic level sensors ................................................ 554
    11.7.2.2 Radar distance measurement .................................................. 555
11.8 Free surface measurements .................................................................. 556
  11.8.1 Optic methods ............................................................................... 556
    11.8.1.1 Optical triangulation ............................................................... 558
    11.8.1.2 Time-of-flight distance measurement .................................... 560
    11.8.1.3 Projection techniques ............................................................. 567
  11.8.2 Acoustic distance measurements ..................................................... 575
    11.8.2.1 Ultrasonic distance measurement using frequency shift-keyed signal ............................................................. 575
    11.8.2.2 Ultrasonic velocity profile meter .......................................... 579
11.9 Summary and final comments ............................................................... 580

Chapter 12 EXISTING HLM FACILITIES FOR EXPERIMENTAL APPLICATIONS... 597
12.1 Introduction ......................................................................................... 597
12.2 Technological facilities and their applications .................................... 597
12.3 Materials testing facilities and their applications ............................... 609
12.4 Thermal-hydraulics facilities and their applications ........................... 640

Chapter 13 SAFETY GUIDELINES ................................................................. 663
13.1 Effects of lead on human health and environment ............................. 664
13.2 Rules and regulations ......................................................................... 667
Chapter 14  PERSPECTIVES AND R&D PRIORITIES OF HEAVY LIQUID METAL COOLANT TECHNOLOGIES ................................................ 679
14.1 Introduction ........................................................................................................ 679
14.2 Technology gaps, R&D needs and priorities for HLM systems operating at temperatures below 600°C ........................................ 680
   14.2.1 HLM thermal-physical properties ...................................................... 681
   14.2.2 HLM chemical properties ................................................................. 681
   14.2.3 Materials ............................................................................................ 681
   14.2.4 Technologies ....................................................................................... 682
   14.2.5 Thermal-hydraulics .......................................................................... 683

List of contributors ............................................................................................................................. 685
List of working group members ......................................................................................................... 687
Chapter 1
INTRODUCTION*

Liquid metals have been studied since the early development of fission energy as reactor core coolants for fast reactors, fusion energy blanket applications and, more recently, for accelerator-driven systems (ADS) proposed for high-level radioactive waste transmutation. Moreover, heavy liquid metals are being proposed as target materials for high power neutron spallation sources.

Accelerator-driven systems (ADS) are nuclear fission reactors with a subcritical core, i.e. $k_{\text{eff}} < 1$. Therefore to operate ADS an external neutron source is needed for a stationary behaviour of the core. A possible external neutron source is provided by a proton accelerator and a spallation target (a heavy liquid metal is often considered). The protons hitting the heavy liquid metal generate neutrons which sustain the chain reaction in the sub-critical core. In Figure 1.1 a schematic view of an accelerator-driven system is provided.

Figure 1.1. Schematic diagram of an ADS [A European Roadmap]

Neutron spallation targets are also being developed to provide a neutron source for other applications. For example, the MEGAPIE spallation neutron target (a schematic view of the MEGAPIE target is shown in Figure 1.2), which will be tested at the SINQ facility of the Paul Scherrer Institut in Switzerland, has been designed and constructed in the frame of ADS development. Its objective is to demonstrate the operability of such a liquid metal target while providing a neutron source for the typical applications at SINQ, i.e. material investigation with neutrons.

* Chapter lead: C. Fazio. For additional contributors, please see the List of Contributors included at the end of this work.
Fast reactors are fission reactors where the neutron spectrum in the core is close to the fission neutron spectrum, since the neutrons are not thermalised as in a conventional light-water-cooled reactor. The fast reactor coolant is appropriately chosen in order to provide an effective heat transfer, without a significant thermalisation of the neutron spectrum. In order to achieve this goal, liquid metals (Na or Pb,Pb/Bi) or gas can be (or have been) used. In Figure 1.3 a schematic view of a Pb-cooled fast reactor is given.

Heavy liquid metals (HLM) such as lead (Pb) or lead-bismuth eutectic (LBE) were proposed and investigated as coolants for fast reactors as early as in the 1950s (e.g. in the USA). Sodium became the preferred choice in the sixties, due to a higher power density achievable with this coolant, which resulted in lower doubling times, an important objective at that time [IAEA TECDOC 1289]. However, LBE was chosen as the coolant for a number of alpha class submarine reactors in the former Soviet Union, which led to very extensive research and development of the coolant technology and materials, with particular emphasis on the chemistry control of the liquid metal to avoid plugging due to slag formation and to enhance corrosion resistance of the steels specifically developed for such services.

More recently, there has been renewed interest in Russia in lead and LBE coolants for civilian fast reactors [Kirillov, 1998, 2000, 2003]. The lead-cooled BREST (Russian acronym for Pb-cooled fast reactor) [Filin, 2000] concept developed since the early 1990s is the most widely known, with the LBE-cooled SVBR (Russian acronym for lead-bismuth fast reactor) concept [Stepanov, 1998] competing for attention. Their features and the associated technologies inspired several projects in the
emerging field of ADS, and in particular lead cooling was associated, in the mid-1990s, with the proposal for an energy amplifier project together with LBE as a spallation target coolant and material. Subsequent development of ADS in the USA, Europe, Japan and the Republic of Korea has adopted a heavy liquid metal (most often LBE) as the coolant for the subcritical core and as coolant and material for the spallation target which provides the external neutron source.

At the Korea Atomic Energy Research Institute (KAERI) and Seoul National University (SNU) in the Republic of Korea, both ADS and LFR systems are under the development in order to explore proliferation-resistant and safe transmutation technology. KAERI has been developing ADS since 1997. KAERI’s ADS, the Hybrid Power Extraction Reactor (HYPER) is designed to transmute TRU and some fission products such as $^{129}$I and $^{99}$Tc. HYPER uses Pb-Bi as both the coolant and target material. At SNU, a Pb-Bi-cooled transmutation reactor, the Proliferation-resistant, Environment-friendly, Accident-tolerant, Continual and Economical Reactor (PEACER) has been developed since 1998.

At SCK•CEN, Belgium, since 1997 studies in the field of lead-bismuth eutectic (LBE) technology have been related to the Multi-purpose Hybrid Research Reactor for High-tech Applications (MYRRHA) project and are aimed at the development of a research reactor driven by an accelerator, where LBE is used as spallation target and coolant.

In Japan, both ADS and LFR systems using LBE are under the development. At the Japan Atomic Energy Research Institute (JAERI) an ADS with the thermal power of 800 MW has been designed, where 250 kg of minor actinides and some long-lived fission products (LLFP) can be transmuted annually. R&D has been conducted on ADS using LBE as a spallation target and a coolant, and research using J-PARC is also planned. The LFR systems using LBE as a coolant have been studied both at Tokyo Institute of Technology (TIT) and the Japan Nuclear Cycle Development Institute (JNC) separately. One of the LFR systems studied at TIT is designated as the Pb-Bi-cooled Direct Contact Water Fast Reactor (PBWFR).

---

1 Now JAEA (Japan Atomic Energy Agency).
In summary, at present a number of experimental programmes are ongoing world-wide for the transmutation of nuclear waste and the development of HLM cooled fast reactors. These include:

- The USA Advanced Fuel Cycle Initiative [Report to Congress, 2003];
- The European Commission four-year (04/2005-04/2009) Integrated Project EUROpean Research Programme for the TRANSmutation of High Level Nuclear Waste in an Accelerator Driven System, IP-EUROTRANS [Integrated Project, 2004], [Knebel, 2005]. In addition in Europe there are several programmes ongoing at national level, as for instance in France the GEDEON, now GEDEPEON (Gestion de Déchets Radioactives par des Options Nouvelle) programme, and the MYRRHA project at SCK•CEN in Belgium. MYRRHA is being developed as a multi-purpose neutron source for R&D applications on the basis of an ADS [Abderrahim, 2001, 2005a, 2005b].
- The South Korean programmes of HYPER (ADS) and PEACER (reactor) [Park, 1996], [Hwang, 2000], [Song, 2004].
- The Japanese programme in the framework of ADS development and LFR development [Mukaiyama, 1999], [Oigawa, 2004], [Sasa, 2004], [Takahashi, 2004].

Finally, in the framework of the Generation-IV Nuclear Energy Systems initiative, a class of Pb/LBE-cooled fast reactors (LFRs) has been chosen as one of six system concepts for further development. A host of new missions have been proposed for LFRs made possible by the properties of Pb/LBE, including hydrogen production, nuclear waste transmutation, and small modular reactors with long-life cores for supplying electricity and heat in remote areas and/or developing economies. In this context a multiyear project at the Idaho National Laboratory and the Massachusetts Institute of Technology investigated medium power lead alloy cooled systems with the aim of producing low cost energy and, at the same time, burning actinides [Todreas, 2004].

In the area of the fusion technology programme the eutectic alloy Pb-17Li is largely studied as breeder and as coolant. A wide range of activities have been conducted in order to characterise materials and develop appropriate technologies [Kleykamp, 2002].

The selection criteria for the use of liquid metals as heat-transfer media in a nuclear environment include the following:

- Neutronics, related to the fast spectrum necessary for breeding, fuel conversion and actinide transmutation in the next generation fast reactors and ADS concepts. In this case the coolant should have:
  - small (fast) capture cross-section (for small parasitic loss of neutrons);
  - high scattering cross-section (for small leakage of neutrons from the core);
  - small energy loss per collision (for small spectrum softening (moderating) effect);
  - high boiling temperature (for prevention of reactivity effects from boiling related coolant voiding).
- Materials:
  - acceptable corrosion and mechanical degradation of structural and containment materials, and lifetime of equipment;
  - high stability of the liquid metal (e.g. limited chemical reactions with secondary coolants and air or formation of spallation products, etc.).
• Thermal-hydraulics:
  – moderate power requirement for circulating the liquid metal;
  – high heat transfer coefficient and small size of heat exchanger.

• Safety:
  – controllable chemical and radioactive hazards;
  – simple and reliable safety measures and systems.

• Economics.

Based on these factors and on the inspection of Table 1.1, it can be concluded that heavy liquid metals are well suited for fast reactor cores (see for example [Todreas, 2004]). Indeed, the use of heavy liquid metals (e.g. Pb/LBE) allow the achievement of a harder neutron spectrum, which results in better neutron economy (essential e.g. for burning actinides). Some other favourable features of using LBE in nuclear systems are based on its high boiling temperature and low melting temperature. The high boiling temperature is an important safety feature, essentially eliminating the pressurisation and boiling concerns while enhancing the inherent safety of reactor cores. Higher allowable operating temperatures also improve efficiency and feasibility of other energy products. The relatively low melting point cases use at low temperatures with reduced risk of uncontrolled freezing. High density and wider range of possible operating temperature offer increased design space for passive safety. A comprehensive comparative assessment of thermo-physical and thermo-hydraulics characteristics of lead, lead-bismuth eutectic alloy and sodium is also given in the IAEA TECDOC 1289.

Table 1.1. Basic characteristics of reactor coolants

<table>
<thead>
<tr>
<th>Coolant</th>
<th>Atomic mass (g/mol)</th>
<th>Relative moderating power</th>
<th>Neutron absorption cross-section (1 MeV) (mbarn)</th>
<th>Neutron scattering cross-sections (barn)</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Chemical reactivity (with air and water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>207</td>
<td>1</td>
<td>6.001</td>
<td>6.4</td>
<td>327</td>
<td>1737</td>
<td>Inert</td>
</tr>
<tr>
<td>LBE</td>
<td>208</td>
<td>0.82</td>
<td>1.492</td>
<td>6.9</td>
<td>125</td>
<td>1670</td>
<td>Inert</td>
</tr>
<tr>
<td>Na</td>
<td>23</td>
<td>1.80</td>
<td>0.230</td>
<td>3.2</td>
<td>98</td>
<td>883</td>
<td>Highly reactive</td>
</tr>
<tr>
<td>H₂O</td>
<td>18</td>
<td>421</td>
<td>0.1056</td>
<td>3.5</td>
<td>0</td>
<td>100</td>
<td>Inert</td>
</tr>
<tr>
<td>D₂O</td>
<td>20</td>
<td>49</td>
<td>0.0002115</td>
<td>2.6</td>
<td>0</td>
<td>100</td>
<td>Inert</td>
</tr>
<tr>
<td>He</td>
<td>2</td>
<td>0.27</td>
<td>0.007953</td>
<td>3.7</td>
<td>–</td>
<td>-269</td>
<td>Inert</td>
</tr>
</tbody>
</table>

Other potentially favourable features of HLM are: lower reactivity associated with hypothetical voiding of the coolant; better shielding against gamma rays and energetic neutrons; high solubility of the actinides in the coolant, which could help to minimise the potential for re-criticality events upon core melting, and no energetic reaction with air and water, thereby eliminating the possibility of fires. One drawback associated with the use of liquid metal coolants, is the potential complexity of in-service inspection and repair.

With respect to spallation neutron sources, there is a general consensus that above 1 MW of beam power, solid targets are hardly feasible from a heat removal point of view. Therefore, liquid metals targets are the best choice (see e.g. [Bauer, 2001]), among the liquid metals lead-alloy-based liquid metal targets are to be preferred if high operating temperatures are required. Properties that make heavy liquid metals ideal as spallation materials for neutron sources are listed in Table 1.2.
Table 1.2. Some relevant properties of possible liquid metal target candidate materials

<table>
<thead>
<tr>
<th>Coolant</th>
<th>Composition (at.%)</th>
<th>Density at 20°C (g/cm³)</th>
<th>Density liquid (g/cm³)</th>
<th>Linear coefficient of thermal expansion 10⁻²/K (solid)</th>
<th>Linear coefficient of thermal expansion 10⁻²/K (400°C)</th>
<th>Volume change upon solidification (%)</th>
<th>Specific heat (J/gK)</th>
<th>Thermal neutron absorption (barn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Elem.</td>
<td>11.35</td>
<td>10.7</td>
<td>2.91</td>
<td>4</td>
<td>3.32</td>
<td>0.14</td>
<td>0.17</td>
</tr>
<tr>
<td>Bi</td>
<td>Elem.</td>
<td>9.75</td>
<td>10.07</td>
<td>1.75</td>
<td>–</td>
<td>-3.35</td>
<td>0.15</td>
<td>0.004</td>
</tr>
<tr>
<td>Pb-Mg eutectic</td>
<td>Pb 97.5% Mg 2.5%</td>
<td>10.6</td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>0</td>
<td>0.15</td>
<td>0.17</td>
</tr>
<tr>
<td>Pb-Bi eutectic</td>
<td>Pb 45% Bi 55%</td>
<td>10.5</td>
<td>10.5</td>
<td>–</td>
<td>0</td>
<td>0</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td>Hg</td>
<td>Elem.</td>
<td>13.55</td>
<td>6.1</td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>0.12</td>
<td>389</td>
</tr>
</tbody>
</table>

The emerging worldwide interests in the applications of HLM coolants have led to many R&D activities in the fields of materials, thermal-hydraulics, physical chemistry, etc. It is becoming increasingly clear and urgent that a HLM handbook is needed for designers of HLM systems and for researchers in this field. Such a handbook should be a comprehensive compilation of all relevant properties, material test results, primary monitoring and control techniques, and instrumentation. Just as important, it should discuss the state of the art in research methodology and R&D resources (test facilities), and suggest a commonly accepted reporting and analysis protocol for systematic advancement of the scientific understanding and technological applications of HLM.

Several liquid metal handbooks dating back to the 1950s with data available at that time have been issued. However, this data was limited due to restrictions associated with strategic national programmes. Although it has been reported that the Russians had a manual or database for designers, this is not publicly available. The US Advanced Accelerator Application (AAA) programme included in its materials handbook a brief chapter on this topic. However, none of these can fulfil the demanding needs of today’s vibrant and diverse international research community.

In this context, the OECD Nuclear Energy Agency (NEA), in the framework of the former Working Party on Partitioning and Transmutation (WPPT), now Working Party on Fuel Cycle (WPFC), launched the HLMC handbook project. The original scope to cover the relatively more mature LBE coolant technology and materials has been expanded to include Pb for higher temperature and high-performance next-generation nuclear systems. The higher availability of basic property data for Pb can serve as a reference, and in some cases, serve as proxy for relatively scarce LBE property data. Conversely, the higher availability of LBE test data and facilities can benefit R&D for Pb. It is also envisioned that this handbook will be an evolving and working document of the continued R&D efforts around the world in the next several years, with increasing utility for designers.

The structure of this handbook is as follows: four chapters are dedicated to HLM properties; the next four chapters cover the materials and testing issues; and the subsequent two chapters summarise the key aspects of the thermal-hydraulics and system technologies. In the last three chapters, other issues such as existing test facilities, safety guidelines and open issues and perspectives are presented.

HLM properties are reported in Chapters 2-5. Chapter 2 compiles the thermo-physical and electrical properties of the LBE and Pb (e.g. density, molar volume, isobaric heat capacity, viscosity, thermal and electrical conductivity, etc.) reported in the open literature. In some cases, significant discrepancies exist among the different sources, and recommendations based on the “best fit” of data are offered.
Chapter 3 addresses the thermodynamic relations, transport properties and chemistry of HLM, such as the solubility and diffusivity of oxygen and metallic elements in the liquid metal. In Chapter 4 the chemistry control and monitoring systems are reported. The main chemistry issue is the monitoring and adjustment of the oxygen level in HLMs for the mitigation of corrosion and coolant contamination problems. For this purpose the development, calibration and performance of electrochemical oxygen sensors and oxygen control systems are extensively described.

Chapter 5 deals with the properties of irradiated LBE and Pb. For this topic, very little data is available and most of them have been produced in the framework of the international MEGAPIE initiative and CERN experiments.

Materials issues are covered in the Chapters 6-9. The compatibility of ferritic/martensitic and austenitic steels with the liquid metals are given in terms of corrosion (Chapter 6) and effects on the mechanical properties in stagnant and flowing liquid metals (Chapter 7). While substantial amount of corrosion test results are available from many sources, most results pertain to relatively short durations (up to a few thousand hours). Although several key qualitative conclusions can be drawn, the wide ranging test conditions and materials render it very difficult at the present to derive a consistent set of correlations for design use, especially in long-term applications. It is also noted that the data on the mechanical property changes is fairly scarce.

In Chapter 8 a collection of data is given representing the combined effect of proton irradiation and HLM on the properties of structural materials. These data have been produced principally at the Paul Scherrer Institute (Switzerland) and in the framework of the MEGAPIE initiative, with contribution from Los Alamos National Laboratory (USA). More data on irradiation effects on compatibility of structural materials with Pb and LBE in the neutron field will be available at the end of the next five-year period, after the completion of the experiments described in this chapter.

Chapter 9 is dedicated to corrosion-protection methods. In particular, two types of methods are under development and testing – the in situ growth and control of a “self-healing” protective oxide layer on the steel surface, and the deposition of a Fe/Al-based surface coating. Other types of coatings, such as in-situ formation of carbides and nitrides via addition of inhibitors, have been tested but not as extensively as the previous one mentioned.

Chapters 10 and 11 address the thermal-hydraulics behaviour and instrumentations needed for scientific, technological and operational purposes. As far as the thermal-hydraulics quantities, it has been seen that the available set of data is still not sufficient for a complete validation of computational fluid dynamics (CFD) codes and for development of reliable and realistic physical models.

A compilation of the existing OECD experimental facilities with their main parameters and key objectives is given in Chapter 12. Chapter 13 briefly reviews the effects of HLM containing Pb and Bi on human and environmental health and safety, and outlines the safety guidelines for the use of HLMs. Finally in Chapter 14 the open issues and the strategic outlook for R&D are summarised.
REFERENCES


Chapter 2
THERMOPHYSICAL AND ELECTRIC PROPERTIES*

2.1 Introduction

Among different heavy liquid metals (HLM), lead (Pb) and three alloys of lead: lead-bismuth eutectic (LBE) 44.5 wt.% Pb + 55.5 wt.% Bi, lead-lithium eutectic 99.32 wt.% Pb + 0.68 wt.% Li, and lead-magnesium eutectic 97.5 wt.% Pb-2.5 wt.% Mg, are considered at present as potential candidates for the coolant of new generation fast reactors (critical and subcritical) and for liquid spallation neutron sources and accelerated driven systems (ADS). LBE is expected to be used in most of ADS projects, mainly due to its low melting temperature of ~397 K (~124°C), resulting in lower corrosion rates and in easier maintenance.

This chapter compiles data on the main thermo-physical properties of molten lead, bismuth and LBE (e.g. density, molar volume, isobaric heat capacity, viscosity, thermal and electrical conductivity, etc.) reported in the open literature. In some cases, significant discrepancies exist among the values given by different sources. Therefore, recommendations based on the “best fit” of data are usually used. Published data on the properties the lead alloys of interest are currently very limited. The main sources are material handbooks published in the 50s and 60s. The first compilations of the main thermophysical properties of Pb and LBE were assembled by [Lyon, 1952], [Kutateladze, 1959], and [Nikolskii, 1959]. In the later handbooks most of data were either reproduced without changes [Mantell, 1958], [Lyon, 1960], [Bonilla, 1964] and [Crean, 1964] or with addition of new results [Friedland, 1966], [Hultgren, 1973, 1974], [Iida, 1988], [Kirillov, 2000], [Gurvich, 1991] and [Cheynet, 1996]. In recent years several review-reports have been published where previous data were reanalysed [Cevolani, 1998], [Imbeni, 1998a, 1998b], [Kyrillov, 2000a, 2000b], [TECDOC-1289, 2002], [Sobolev, 2002, 2005, 2007]. These data and a many of the recommendations and conclusions in this chapter are mainly based on these later reports. Some publications issued in the former Soviet Union and recent Russian compilation reports are not taken into account in this version of Chapter 2 because of difficulties in receiving them.

The reliability of data depends on the method used for production and the care with which the method is used. In general, data concerning metals in the liquid or vapour state show a significant dispersion, with the exception of the melting points. Only a few authors of compilations have paid adequate attention to dispersion and standard deviation of their reported values [Hultgren, 1973, 1974].

The database in this chapter is presented in the form of a set of tables. Each table is devoted to one parameter and contains information about the references used, year of publication, measurement method, precision, temperature range, and composition of a sample. Moreover, values of the parameter from the reference and correlation obtained on the basis of the available data are given. Often it was not possible to access the original sources of data. In this case, the data selected from handbooks and

* Chapter leads: V. Sobolev (SCK•CEN, Belgium), G. Benamati (ENEA, Italy). For additional contributors, please see the List of Contributors included at the end of this work. The authors acknowledge Dr. N. Li, Dr. H.U. Borgstedt, Prof. R. Ballinger, Dr. C. Latgé and Dr. H. Katsuta for fruitful discussions and useful suggestions, and Dr. W. Pfrang for some important remarks.
other compilations were used to fill in the database. In the case where information concerning precision
or/and method was not available, a question mark (?) is used to indicate that the data should be used
with caution. In all recommended correlations, temperature is given in degrees of Kelvin (“kelvins”).

2.2 Pb-Bi alloy phase diagram

One of the first more or less complete phase diagrams for the binary Pb-Bi system was published
in the handbook of G.O. Hiers [Hiers, 1948] and reproduced later in the well-known Smithells Metal
Reference Book [Smithells, 1955]. This phase diagram is presented in Figure 2.2.1 below. (It was
reproduced almost without changes in the book of B. Ageron, et al. [Ageron, 1959] and in the later
editions of the Smithells Metal Reference Book [Smithells, 1983, 2004].)

Figure 2.2.1. Phase diagram of the Pb-Bi system [Smithells, 1955]

This diagram shows:

- an eutectic point at 55.5 wt.% Bi with a melting temperature of 124°C (397 K);
- a peritectic point at 32.2 wt.% Bi with a melting temperature of 184°C (457 K);
- the solubility limits in solid state: 21.5 wt.% Bi in Pb (α-phase region) and 0.5 wt.% Pb in Bi
  (γ-phase region);
- intermetallic compound phase (β-phase region);
- liquidus and solidus lines.
M. Hansen and K. Anderko [Hansen 1958] presented the Pb-Bi phase diagram with some new experimental results. This diagram with additional revisions was reported in [Elliott 1965]. Some parameters were changed in comparison with the diagram reproduced in Figure 2.2.1 as follows:

- the eutectic point at 56.7 wt.% Bi (56.3 at.% Bi) with a melting temperature of 124.7°C (398 K);
- the peritectic point at 36.2 wt.% Bi (36 at.% Bi);
- the solubility limits in the solid state are reported to be 23.4 wt.% (23.3 at.%) Bi in Pb.

In 1973, the Pb-Bi phase diagram with refinements of the boundaries of the $\epsilon$-phase, given by B. Predel and W. Schwerman [Predel, 1967], and boundaries of $\gamma$(Bi)-phase, given by M.V. Nosek, et al. [Nosek, 1967], was published by R. Hultgren, et al. [Hultgren, 1973]. This diagram is reproduced in Figure 2.2.2 below.

Figure 2.2.2. Phase diagram of the Pb-Bi system [Hultgren, 1973]

This diagram provides the same eutectic and peritectic points as those proposed by [Elliott 1965], but gives:

- the melting point of Bi at 271.22°C (544.52 K);
- the melting point of Pb at 327.3°C (600.6 K);
- the solubility limit of Pb in Bi in the solid state – 5 at.%;
- the solubility limit of Bi in Pb in the solid state – 24 at.%;
- an eutectoid point at 72.5 at.% Pb and -46.7°C (227 K);
- $\epsilon$-phase region.
In 1992 N.A. Gokcen [Gokcen, 1992] proposed a few modifications for some characteristic points (Figure 2.2.3):

- more precise melting points of elements: \( T_{\text{melt Bi}} = 271.442^\circ \text{C} (544.592 \text{ K}) \); \( T_{\text{melt Pb}} = 327.502^\circ \text{C} (600.652 \text{ K}) \);
- the eutectic point at 45.0 at.% Pb and \( T_{\text{melt LBE}} = 125.5^\circ \text{C} (398.65 \text{ K}) \);
- the peritectic point at 71 at.% Pb and 187°C (460.15 K);
- the lower limits of the elements solubility in the solid state – 0.5 at.% Pb in Bi and 22 at.% Bi in Pb.

These modifications were reproduced in a Pb-Bi phase diagram published in the ASM Handbook of 1992 [Baker, 1992].

**Figure 2.2.3. Phase diagram of the Pb-Bi system [Gokcen, 1992]**

In many Russian publications (e.g. [Orlov 1997, 2003]), followed recently by other authors, a phase-diagram is often presented which gives the LBE eutectic composition at 55.5 wt.% Bi and 44.5 wt.% Pb with the eutectic melting temperature of 123.5°C (396.65 K); the temperature is probably reproduced from [Kutateladze, 1959].

**Recommendation**

The phase diagram of N.A. Gokcen [Gokcen, 1992] is recommended for use in engineering and design calculations with the exception of the eutectic point which will be considered in the next section.
2.3 Normal melting point

2.3.1 Lead

The values of the lead and bismuth melting temperatures were found in the following handbooks [Lyon, 1954, 1960], [Kutateladze, 1959], [Hofmann, 1970], [Hultgren, 1974], [Lucas, 1984], [Iida, 1988], [Kubaschewski, 1979, 1993], [Gocksen, 1992], [Cheynet, 1996] and [Smithells, 2004].

Friedland [Friedland, 1966] reproduced the values of the melting points from Lyon [Lyon, 1954, 1960]. The compilation [Imbeni, 1998a] presented data on the lead and bismuth melting temperatures from different sources with the conclusion that dispersion is not large. In the handbook [Kyrillov, 2000a] and in the IAEA report [TECDOC-1289, 2002] the lead melting temperature presented in earlier compilations [Kutateladze, 1959] was repeated. These sources have not been included in the database on the melting point.


The data for the melting temperature of lead and bismuth, extracted from the above selected sources, are presented in Tables 2.3.1 and 2.3.2 respectively.

All selected data yield approximately the same value within their error limits. The most probable value for the melting temperature of technically pure lead obtained on the basis of the data presented in the table is:

\[ T_{melt \, Pb} = 600.6 \pm 0.1 \text{ K} \]  

(2.1)

The melting point of lead increases by 0.0792 K per 1 MPa when pressure increases from about 15 up to 200 MPa. The increase continues at a lower rate, 0.0671 K per 1 MPa, in the range of 800-1200 MPa, and an increase of 5.4 K for a pressure increase from about 2 to 3 GPa was cited in [Hoffman, 1970].

2.3.2 Bismuth

The database for the melting point of bismuth are extracted from about the same sources as for lead and is presented in Table 2.3.2.

For the melting temperature of bismuth there is uncertainty in the cited data in the first digit after the decimal point. Therefore the recommended mean value is as follows:

\[ T_{melt \, Bi} = 544.4 \pm 0.3 \text{ K} \]  

(2.2)
<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1.1</td>
<td>Melting temperature</td>
<td>Temperature vs. power</td>
<td>0.1°C</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>327.4°C</td>
<td>[Lyon, 1954]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1.2</td>
<td>Melting temperature</td>
<td>Temperature vs. power</td>
<td>0.1°C</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>327.4°C</td>
<td>[Kutateladze, 1959]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1.3</td>
<td>Melting temperature</td>
<td>n/a</td>
<td>0.1°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>327.3°C</td>
<td>[Hofmann, 1970]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1.4</td>
<td>Melting temperature</td>
<td>Temperature vs. power</td>
<td>0.1°C</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>600.6 K</td>
<td>[Hultgren, 1974]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1.5</td>
<td>Melting temperature</td>
<td>?</td>
<td>0.05 K</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>600.55 K</td>
<td>[Iida, 1988]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1.6</td>
<td>Melting temperature</td>
<td>?</td>
<td>0.005°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>327.502°C</td>
<td>[Gokcen, 1992]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1.7</td>
<td>Melting temperature</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>601 K</td>
<td>[Kubaschewski, 1993]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1.8</td>
<td>Melting temperature</td>
<td>?</td>
<td>0.1°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>327.4°C</td>
<td>[Cheynet, 1996]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1.9</td>
<td>Melting temperature</td>
<td>?</td>
<td>0.005°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>327.462°C</td>
<td>[Smithells, 2004]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.3.2. Database on the normal melting point of bismuth

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.1</td>
<td>Melting temperature</td>
<td>Temperature vs. power</td>
<td>0.1°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>271.0°C</td>
<td>[Lyon, 1954]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $T_{melt} = 544.15$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2.2</td>
<td>Melting temperature</td>
<td>Temperature vs. power</td>
<td>1°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>271°C</td>
<td>[Kutateladze, 1959]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $T_{melt} = 544.15$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2.3</td>
<td>Melting temperature</td>
<td>Temperature vs. power</td>
<td>0.05 K</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>544.52 K</td>
<td>[Hultgren, 1974]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $T_{melt} = 544.52$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2.4</td>
<td>Melting temperature</td>
<td>?</td>
<td>1 K (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>545 K</td>
<td>[Kubaschewski, 1993]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $T_{melt} = 545$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2.5</td>
<td>Melting temperature</td>
<td>?</td>
<td>0.05 K</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>544.10 K</td>
<td>[Iida, 1988]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $T_{melt} = 544.10$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2.6</td>
<td>Melting temperature</td>
<td>?</td>
<td>0.005°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>271.442°C</td>
<td>[Gokcen, 1992]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $T_{melt} = 544.592$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: High purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2.7</td>
<td>Melting temperature</td>
<td>?</td>
<td>0.05°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>271.40°C</td>
<td>[Smithells, 2004]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $T_{melt} = 544.55$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: High purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.3.3 LBE

The sources of data for the LBE melting point included in this handbook are [Lyon, 1954], [Kutateladze, 1959], [Hultgren, 1973], [Smithells, 1955], [Eliot, 1965] and the ASM Handbook [Baker, 1992]. These data were reproduced in later handbooks [Lyon, 1960], [Kyrillov, 2000a], [Smithells, 1983] and compilations [Cevolani, 1998], [Imbeni, 1998b], [TECDOC-1289, 2002], [Sobolev, 2002]. The selected sources included in the database (Table 2.3.3) give for the LBE melting temperature $T_{melt} = 123.5-125.5$°C (396.7-398.7 K) at normal atmospheric pressure.

The mean value of:

$$T_{melt \text{ LBE}} = 397.7 \pm 0.6 \text{ K} \quad (2.3)$$

is recommended on the basis of the data presented in Table 2.3.3.
### Table 2.3.3. Database on the LBE normal melting point

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.1</td>
<td>Melting temperature</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>125°C</td>
<td></td>
<td>Lyon, 1954</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: T\text{melt} = 398.15 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.2</td>
<td>Melting temperature</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>123.5°C</td>
<td></td>
<td>Kutateladze, 1959</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: T\text{melt} = 396.65 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.3</td>
<td>Melting temperature</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>398 K</td>
<td></td>
<td>Hultgren, 1973</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: T\text{melt} = 398 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 43.7 at.% Pb + 56.3 at.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.4</td>
<td>Melting temperature</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>124°C</td>
<td></td>
<td>Smithells, 1955</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: T\text{melt} = 397.15 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.8 wt.% Pb + 55.2 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.5</td>
<td>Melting temperature</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>125°C</td>
<td></td>
<td>Eliot, 1965</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: T\text{melt} = 398.15 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 43.7 at.% Pb + 56.3 at.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3.6</td>
<td>Melting temperature</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>125.5°C</td>
<td></td>
<td>Gokcen, 1992</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: T\text{melt} = 398.65 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 45.0 at.% Pb + 55.0 at.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 2.4 Volume change at melting and solidification

A detailed knowledge of volume changes in metals and alloys at their melting points is of critical importance in the understanding of solidification processes.

- **Solid lead.** Similar to the majority of metals with the FCC crystal structure, lead exhibits a volume increase upon melting. At normal conditions a volume increase of 3.81% has been observed in pure lead [Iida, 1988]. In several engineering handbooks a value of ~3.6% is often given for lead of technical purity [Lyon, 1954, 1960], [Kyrillov, 2002].

- **Solid bismuth.** Solid bismuth shows a volume contraction during melting, similar to other semimetals. The anisotropic rigid bonds are apparently broken on melting, and the neighbouring atoms are packed closer one to another. According to [Iida, 1988], pure bismuth contracts approximately 3.87% upon melting. A contraction of 3.32% was reported by [Lyon, 1954, 1960] and a value of ~3.3% was recommended in an IAEA report [Kyrillov, 2002] for Bi-coolant.

- **LBE.** A negligible volume change on melting of solid LBE at normal atmospheric pressure has been published in the handbook of Lyon [Lyon, 1954]. This recommendation has been repeated in later handbooks and compilations (e.g. [Kyrillov, 2002], [Sobolev, 2002]).
Recommendations for the mean values of the volume change upon melting are summarised for Pb, Bi and LBE in Table 2.4.1. It is recommended that for very slow melting (quasi-equilibrium conditions) the volume change upon melting is close to zero for LBE.

Table 2.4.1. Volume change of pure lead, bismuth and LBE at melting

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Bi</th>
<th>LBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta V_m/V_m$</td>
<td>+3.7</td>
<td>-3.7</td>
<td>~0.0</td>
</tr>
</tbody>
</table>

The situation is more complicated for LBE freezing and melting accompanied by rapid temperature change. In the handbook of Lyon [Lyon, 1954] a 1.43 vol.% contraction of LBE on freezing with a subsequent expansion of the solid of 0.77 vol.% at an arbitrary temperature of 65°C has been reported. A contraction of 1.52±0.1 vol.% of the solid phase after solidification of LBE has also been mentioned in [Hofmann, 1970]. The results of measurements of LBE expansion over time at room temperature after solidification and rapid cooling has been reported by H. Glasbrenner et al. [Glasbrenner, 2005]. In these results, shown in Figure 2.4.1, one can see that after solidification and cooling the studied material contracted about 0.35%. After about 100 minutes of exposure at room temperature, its volume returns to the initial value, but after one year its linear size increases by about 1.2%.

The problems of freezing and melting of LBE in the reactor circuits were analysed by [Pylchenkov, 1999]. He pointed out that the results of the freezing/de-freezing experiments are very sensitive to the experimental conditions and that very long times (>100 d) are usually required to reach equilibrium. Some of his results are shown in Figure 2.4.2. The volume effect upon freezing/de-freezing depends very strongly on phase-structure of local transformations in the solid state related to the mutual solubility of LBE components (Figure 2.2.1). A negligible volume change has been observed in some experiments. According to E.H. Pylchenkov [Pylchenkov 1999], post-solidification expansion may occur in a metastable alloy as a result of local changes in the composition. An excess in $\gamma$-phase precipitation during freezing can result in a volume increase.

Figure 2.4.1. Linear expansion of LBE as a function of time after solidification and cooling down to room temperature [Glasbrenner 2005]
H. Glasbrenner [Glasbrenner, 2005] showed that re-crystallisation at the level of a crystal grain is responsible for the expansion of LBE after freezing. In their experiments, two phases were identified immediately after rapid solidification of LBE:

- \( \beta \)-phase: an intermetallic compound with 42 at.% Bi (at the freezing point) and a hexagonal closed packed structure;
- \( \gamma \)-phase: a solid solution of Pb in Bi (~0.4 at.%Pb) with a rhombohedric structure.

The \( \beta \)-phase formed at freezing is not stable at room temperature. With time it is partly transformed into a \( \beta \)-phase with a lower Bi content (about 35 at.%) and \( \gamma \)-phase [Takeda, 1997], [Agostini, 2004]. As the \( \gamma \)-phase needs much more space, the transformation produces an expansion of the material.

Measurements of this kind of LBE expansion performed at room temperature [Gröschel, 2005] showed that it is reduced by a factor of 6 when slow cooling is used to 60-90°C (333.3-363.3 K) in the place of quenching. Moreover, Takeda’s experiments [Takeda, 1997] showed that the first period of a faster expansion [which ranges from 2 h at 110°C (383.3 K) to three months at 20°C (293.3 K)] is followed by a second one with a lower expansion rate. The final increase in volume rarely exceeds 1.3% in one year.

Pylchenkov [Pylchenkov, 1999] pointed out the general tendency: the volume effect of LBE melting-solidification is minimal for pure eutectic materials.
2.5 Latent heat of melting at the normal melting point

2.5.1 Lead

The heat of melting of lead and bismuth at the normal melting point (the enthalpy change on melting) was taken from about the same sources as for the melting temperature: [Lyon 1954], [Hultgren, 1974], [Cheynet, 1996], [Kubaschewski, 1993], [Iida, 1988], [Lucas, 1984], and from the IAEA report [TECDOC-1289, 2002]. The selected database is presented in Tables 2.5.1 and 2.5.2 below. The value of the bismuth latent heat of melting from Cheynet [Cheynet, 1996] has not been included in the database because it was extracted from the same source as that of Hultgren [Hultgren, 1974].

Table 2.5.1. Database on the latent heat of melting of lead at the normal melting point

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1.1</td>
<td>Heat of melting</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10⁵ (?)</td>
<td>5.89 cal/g</td>
<td>[Lyon, 1954]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Interpolation function: ( Q_{\text{melt}} = 24.7 ) kJ/kg = 5.11 kJ/mole</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
</tr>
<tr>
<td>5.1.2</td>
<td>Heat of melting</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10⁵ (?)</td>
<td>24.7 kJ/kg</td>
<td>[TECDOC-1289, 2002]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Interpolation function: ( Q_{\text{melt}} = 24.7 ) kJ/kg = 5.11 kJ/mole</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
</tr>
<tr>
<td>5.1.3</td>
<td>Heat of melting</td>
<td></td>
<td></td>
<td>42 J/mole</td>
<td>n/a</td>
<td>4799 J/mole</td>
<td>[Hultgren, 1974]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Interpolation function: ( Q_{\text{melt}} = 23.2 ) kJ/kg = 4.80 kJ/mole</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
</tr>
<tr>
<td>5.1.4</td>
<td>Heat of melting</td>
<td>?</td>
<td>0.5 kJ/mole (?)</td>
<td>n/a</td>
<td>~ 10⁵ (?)</td>
<td>4.8 kJ/mole</td>
<td>[Kubaschewski, 1993]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Interpolation function: ( Q_{\text{melt}} = 23 ) kJ/kg = 4.8 kJ/mole</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
</tr>
<tr>
<td>5.1.5</td>
<td>Heat of melting</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10⁵ (?)</td>
<td>4.81 kJ/mol</td>
<td>[Iida, 1988]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Interpolation function: ( Q_{\text{melt}} = 23.2 ) kJ/kg = 4.81 kJ/mole</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
</tr>
<tr>
<td>5.1.6</td>
<td>Heat of melting</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10⁵ (?)</td>
<td>5109 J/mol</td>
<td>[Lucas, 1984]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Interpolation function: ( Q_{\text{melt}} = 24.7 ) kJ/kg = 5.11 kJ/mole</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
</tr>
<tr>
<td>5.1.7</td>
<td>Heat of melting</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10⁵ (?)</td>
<td>4.76 kJ/mole</td>
<td>[Cheynet, 1996]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Interpolation function: ( Q_{\text{melt}} = 23.0 ) kJ/kg = 4.76 kJ/mole</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Comments: Unknown purity</td>
</tr>
</tbody>
</table>

The selected values for lead lie in the range of 4.76-5.11 kJ/mole. The mean value and the mean deviation are:

\[
Q_{\text{melt} \ Pb} = 4.9 \pm 0.2 \text{ kJ/mole} = 23.8 \pm 0.7 \text{ kJ/kg}
\]  
(2.4)

These values are recommended for the latent heat of melting of the pure lead at the normal melting point.
2.5.2 Bismuth

The database for the latent heat of melting of bismuth is presented in Table 2.5.2.

Table 2.5.2. Database on the latent heat of melting of bismuth at the normal melting point

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2.1</td>
<td>Heat of melting</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>12.0 cal/g</td>
<td>Lyon, 1954</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: $Q_{\text{melt}} = 50.2 \text{ kJ/kg} = 10.5 \text{ kJ/mole}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2.2</td>
<td>Heat of melting</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>54.7 kJ/kg</td>
<td>TECDOC-1289, 2002</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: $Q_{\text{melt}} = 54.7 \text{ kJ/kg} = 11.4 \text{ kJ/mole}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2.3</td>
<td>Heat of melting</td>
<td>?</td>
<td>209 J/mole</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>11297 J/mole</td>
<td>Hultgren, 1974</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: $Q_{\text{melt}} = 54.1 \text{ kJ/kg} = 11.3 \text{ kJ/mole}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2.4</td>
<td>Heat of melting</td>
<td>?</td>
<td>0.5 kJ/mole (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>11.3 kJ/mole</td>
<td>Kubaschewski, 1993</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: $Q_{\text{melt}} = 54.1 \text{ kJ/kg} = 11.3 \text{ kJ/mole}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2.5</td>
<td>Heat of melting</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>10.89 kJ/mol</td>
<td>Iida, 1988</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: $Q_{\text{melt}} = 52.1 \text{ kJ/kg} = 10.9 \text{ kJ/mole}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2.6</td>
<td>Heat of melting</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>10.5 kJ/mol</td>
<td>Lucas, 1984</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: $Q_{\text{melt}} = 50.2 \text{ kJ/kg} = 10.5 \text{ kJ/mole}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the case of Bi, the difference between the maximum and minimum values of the heat of melting is about 0.8 kJ mol$^{-1}$. The mean value and the mean deviation are:

\[
Q_{\text{melt Bi}} = 11.0 \pm 0.4 \text{ kJ/mole} = 52.6 \pm 1.7 \text{ kJ/kg} \quad (2.5)
\]

This value is recommended for the latent heat of melting of the pure bismuth at the normal melting point.

2.5.3 LBE

The most cited results for the heat of melting of LBE at normal atmospheric pressure were published in the handbook edited by Friedland [Friedland, 1966]. The recent IAEA compilation [TECDOC-1289, 2002] probably reproduces the value of the melting heat from [Kyrillov, 2000b]. The data from these sources are included in Table 2.5.3.

The mean value for the LBE melting heat of:

\[
Q_{\text{melt LBE}} = 8.01 \pm 0.07 \text{ kJ/mole} = 38.5 \pm 0.3 \text{ kJ/kg} \quad (2.6)
\]

is the recommended value at normal atmospheric pressure.
Table 2.5.3. Database on the latent heat of melting of LBE fusion at the normal melting point

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy %</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3.1</td>
<td>Heat of melting</td>
<td>?</td>
<td>n/a</td>
<td>~ $10^{5}$ (?)</td>
<td></td>
<td>38134 J kg$^{-1}$</td>
<td>[Friedland, 1966]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: $Q_{\text{melt}} = 38.134 \text{kJ/kg} = 7.939 \text{kJ/mole}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.3.2</td>
<td>Heat of melting</td>
<td>?</td>
<td>n/a</td>
<td>~ $10^{5}$ (?)</td>
<td></td>
<td>38.8 kJ kg$^{-1}$</td>
<td>[TECDOC-1289, 2002]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: $Q_{\text{melt}} = 38.8 \text{kJ/kg} = 8.08 \text{kJ/mole}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.6 Normal boiling point

2.6.1 Lead

For the boiling temperature of lead and bismuth at normal pressure, the same sources were used as for their melting temperature: [Lyon, 1954], [Kutateladze, 1959], [Hultgren, 1974], [Lucas, 1984], [Iida, 1988], [Kubaschevski, 1993], [Cheynet, 1996] and [Smithells, 2004], plus, the handbook edited by Howe [Howe, 1961] and the recent IAEA report [TECDOC-1289, 2002].

The data for the boiling temperatures of lead and bismuth extracted from the above-mentioned sources are presented in Tables 2.6.1 and 2.6.2 respectively.

The variation in the lead boiling temperature between the selected sources is more than for the melting temperature and is a large as 25 K. The most probable value of:

$$T_{\text{boil Pb}} = 2016 \pm 10 \text{ K} \quad (2.7)$$

is recommended for the boiling temperature of technically pure lead at normal conditions, based on an analysis of the data in Table 2.6.1.

2.6.2 Bismuth

The database on the normal boiling point of bismuth is presented in Table 2.6.2.

A significant level of uncertainty exists for the boiling point of bismuth with a range of about 150 K between the maximum and the minimum. Therefore the following mean value and the mean deviation, while uncertain, is recommended for the boiling temperature of technically pure bismuth at normal conditions:

$$T_{\text{boil Bi}} = 1806 \pm 50 \text{ K} \quad (2.8)$$

2.6.3 LBE

The boiling point of LBE at normal atmospheric pressure is given in the handbook of Lyon [Lyon, 1954], and by Kutateladze [Kutateladze, 1959]. Both sources give the same value of
Table 2.6.1. Database on the normal boiling point of lead

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1.1</td>
<td>Boiling temp.</td>
<td>Temperature vs. power</td>
<td>10°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1737°C</td>
<td>[Lyon, 1954]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 2010 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.1.2</td>
<td>Boiling temp.</td>
<td>Temperature vs. power</td>
<td>10°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1740°C</td>
<td>[Kutateladze, 1959]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 2013 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.1.3</td>
<td>Boiling temp.</td>
<td>Temperature vs. power</td>
<td>5°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1749°C</td>
<td>[Smithels, 2004]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 2022 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.1.4</td>
<td>Boiling temp.</td>
<td>?</td>
<td>5°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1745°C</td>
<td>[TECDOC-1289, 2002]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 2018 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.1.5</td>
<td>Boiling temp.</td>
<td>?</td>
<td>5°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1750°C</td>
<td>[Iida, 1988]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 2023 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.1.6</td>
<td>Boiling temp.</td>
<td>?</td>
<td>5°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1737°C</td>
<td>[Cheynet, 1996]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 2010 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.6.2. Database on the normal boiling point of bismuth

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2.1</td>
<td>Boiling temp.</td>
<td>Temperature vs. power</td>
<td>10°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1477°C</td>
<td>[Lyon, 1954]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 1750 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.2.2</td>
<td>Boiling temp.</td>
<td>Temperature vs. power</td>
<td>10°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1490°C</td>
<td>[Kutateladze, 1959]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 1763 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.2.3</td>
<td>Boiling temp.</td>
<td>Temperature vs. power</td>
<td>10°C</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1564°C</td>
<td>[Smithells, 2004]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 1837 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.2.4</td>
<td>Boiling temp.</td>
<td>?</td>
<td>5°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1627°C</td>
<td>[Howe, 1961]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 1900 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.2.5</td>
<td>Boiling temp.</td>
<td>?</td>
<td>5 K</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1833 K</td>
<td>[Iida, 1988]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 1833 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.2.6</td>
<td>Boiling temp.</td>
<td>?</td>
<td>5°C (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>1737°C</td>
<td>[Cheynet, 1996]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: T_{b_{\text{lead}}} = 1750 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
This value was reproduced later in other publications (e.g. [Friedland, 1966], [Hultgren, 1973], [TECDOC-1289, 2002]). However, in the handbook of Lyon [Lyon, 1954] it is mentioned that in the original source $T_{\text{boil LBE}} = 1677^\circ C (1950 K)$ was also cited. The recommendations [Lyon, 1954] and [Kutateladze, 1959] have been included in the database presented in Table 2.6.3.

Table 2.6.3. Database on the LBE normal boiling point

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3.1</td>
<td>Boiling temp.</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>$\sim 10^5 (?)$</td>
<td>1670°C</td>
<td>[Lyon, 1954]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: $T_{\text{boil}} = 1670^\circ C = 1943 K$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.3.2</td>
<td>Boiling temp.</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>$\sim 10^5 (?)$</td>
<td>1670°C</td>
<td>[Kutateladze, 1959]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: $T_{\text{boil}} = 1670^\circ C = 1943 K$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
</tr>
</tbody>
</table>

Based on the results of Table 2.6.3, and assuming that uncertainty is the same as for the bismuth boiling temperature, the value of:

$$T_{\text{boil LBE}} = 1943 \pm 50 K$$  \hspace{1cm} (2.9)

is recommended for the normal boiling temperature of the technically pure LBE.

2.7 Heat of vaporisation at the normal boiling point

The latent heat (enthalpy) of vaporisation is a measure of the cohesive energy of atoms in a liquid metal. Therefore, it correlates with surface tension and thermal expansion.

2.7.1 Lead

The information on the latent heat of vaporisation of lead and bismuth at the normal boiling point (the enthalpy change on boiling) is not numerous. The following sources were included in the database: [Lyon, 1954], Smithells Metals Reference Book [Smithells, 1983], [Iida, 1988], [Lucas, 1984], and the recommendations of the IAEA report [TECDOC-1289, 2002]. The selected database is presented in Tables 2.7.1 and 2.7.2.

The literature values are very close, with the difference between maximum and minimum values less than 1%. The mean value and the mean deviation are:

$$Q_{\text{boil Pb}} = 177.8 \pm 0.4 \text{ kJ/mole} = 858.2 \pm 1.9 \text{ kJ/kg}$$  \hspace{1cm} (2.10)

These values are recommended for the latent heat of vaporisation for pure lead at the normal boiling point.

2.7.2 Bismuth

The database for the latent heat of vaporisation of molten bismuth at the normal boiling point is presented in Table 2.7.2.
### Table 2.7.1. Database on the latent heat of vaporisation of lead at the normal boiling point

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1.1</td>
<td>Heat of boiling</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>204.6 cal/g</td>
<td>[Lyon, 1954]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 856.7 \text{ kJ/kg} = 177.5 \text{ kJ/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.1.2</td>
<td>Heat of boiling</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>856.8 kJ/kg</td>
<td>[TECDOC-1289, 2002]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 856.8 \text{ kJ/kg} = 177.5 \text{ kJ/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.1.3</td>
<td>Heat of boiling</td>
<td>?</td>
<td>1 kJ/mole (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>178 kJ/mole</td>
<td>[Iida, 1988]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 859 \text{ kJ/kg} = 178 \text{ kJ/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.1.4</td>
<td>Heat of boiling</td>
<td>?</td>
<td>1 kJ/mole (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>177.5 kJ/mole</td>
<td>[Lucas, 1984]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 856.8 \text{ kJ/kg} = 177.5 \text{ kJ/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.1.5</td>
<td>Heat of boiling</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>178.8 kJ/mol</td>
<td>[Smithells, 1983]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 862.9 \text{ kJ/kg} = 178.8 \text{ kJ/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2.7.2. Database on the heat of vaporisation of bismuth at the normal boiling point

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2.1</td>
<td>Heat of boiling</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>204.3 cal/g</td>
<td>[Lyon, 1954]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 855.4 \text{ kJ/kg} = 178.8 \text{ kJ/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.2.2</td>
<td>Heat of boiling</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^7 (?)</td>
<td>852 kJ/kg</td>
<td>[TECDOC-1289, 2002]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 852 \text{ kJ/kg} = 178.1 \text{ kJ/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.2.3</td>
<td>Heat of boiling</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>178.6 J/mole</td>
<td>[Smithells, 1983]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 857.4 \text{ kJ/kg} = 179.2 \text{ kJ/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.2.4</td>
<td>Heat of boiling</td>
<td>?</td>
<td>0.1 kJ/mole (?)</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>194 kJ/mole</td>
<td>[Iida, 1988]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 928 \text{ kJ/kg} = 194 \text{ kJ/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.2.5</td>
<td>Heat of boiling</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>J/mol</td>
<td>[Lucas, 1984]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 855.5 \text{ kJ/kg} = 178.8 \text{ kJ/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The mean value and the mean deviation are:

\[ Q_{\text{boil Bi}} = 181 \pm 4 \text{ kJ/mole} = 857 \pm 20 \text{ kJ/kg} \]  \hspace{1cm} (2.11)

These values are recommended for the latent heat of vaporisation of pure bismuth at the normal boiling point.

### 2.7.3 LBE

A value of 178.352 kJ/mol was published in the handbook of Friedland [Friedland, 1966] for the latent heat of vaporisation of LBE at the normal boiling point. The more recent IAEA compilation [TECDOC-1289, 2002] recommends a value of 177 kJ/mol. These two sources were included in the database and are listed in Table 2.7.3.

#### Table 2.7.3. Database on the heat of vaporisation of LBE at the normal boiling point

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy %</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3.1</td>
<td>Heat of boiling</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>178352 J/mole</td>
<td>[Friedland, 1966]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 856722 \text{ J/kg} = 178352 \text{ J/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: ?</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.3.2</td>
<td>Heat of boiling</td>
<td>?</td>
<td>?</td>
<td>n/a</td>
<td>~ 10^5 (?)</td>
<td>852 J/kg</td>
<td>[TECDOC-1289, 2002]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( Q_{\text{boil}} = 852 \text{ J/kg} = 177 \text{ J/mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The mean values of:

\[ Q_{\text{boil LBE}} = 178.0 \pm 0.4 \text{ kJ/mole} = 854 \pm 2 \text{ kJ/kg} \]  \hspace{1cm} (2.12)

are recommended for the latent heat of vaporisation of the pure LBE at the normal boiling point.

### 2.8 Saturation vapour pressure

The vapour pressure of a liquid metal is an important property which is directly related to the latent heat of evaporation (cohesive energy). For the equilibrium between liquid (\( l \)) and vapour (\( v \)) phases, the Clausius-Clapeyron equation states that:

\[
\frac{dp}{dT} = \frac{H_v - H_l}{T(V_v - V_l)}
\]  \hspace{1cm} (2.13)

Therefore, assuming that the vapour behaves as a perfect gas and neglecting the volume of liquid in comparison with that of the gas, it can be obtained that:

\[
p = A \cdot \exp \left( -\frac{\Delta H}{RT} \right)
\]  \hspace{1cm} (2.14)

where \( A \) is a constant of integration and \( \Delta H \) is the heat (enthalpy) of evaporation.
The above equation can provide approximate values for equilibrium vapour pressures over a wide range of temperature due to the relatively small variation of $\Delta H$ with temperature. Closer fits of the experimental results can sometimes be obtained by adding supplementary temperature dependent terms.

2.8.1 Lead

The data for the saturation vapour pressure of lead at different temperatures were found in the following publications: [Lyon, 1954, 1960], [Friedland, 1966], [Hultgren, 1974], in the Smithells Metals Reference Book [Smithells, 1893, 2004], in the compilations of B. Cheynet [Cheynet, 1996] and of O. Kubaschewski, et al. [Kubaschewski, 1993] reproduced in [Iida, 1988].


Data reported by J.R. Weeks [Weeks, 1971] were taken from [Lyon, 1954, 1960] and [Smithells, 1955], therefore they were not included in the database.

Figures 2.8.1 and 2.8.2 show the values of vapour pressure and deviation of molten lead, respectively, taken from the above cited literature and plotted as a function of temperature. It can be seen that, at first view, the agreement among the different sources is satisfactory. Using the selected data and Eq. (2.14) as a first approach, the following correlation was obtained for the saturated vapour pressure of molten lead where temperature is in kelvins:

$$p_s = 6.189 \times 10^9 \cdot \exp\left(-\frac{22216}{T}\right)$$  \hspace{1cm} (2.15)

The deviation of the selected literature data on the saturated vapour pressure of lead from the recommended correlation (2.15) is plotted in Figure 2.8.2. One can see that agreement is rather good and the deviation is about 12-15% (except the low temperature points of [Hultgren 1974]). Under these circumstances, there is no need for a more precise correlation. Therefore relationship (2.15) is recommended for estimation of the saturated vapour pressure of lead from the melting temperatures up to the normal boiling point.

2.8.2 Bismuth


Figures 2.8.3 shows the values for the saturated vapour pressure of molten bismuth from the above cited sources plotted as a function temperature.
Figure 2.8.1. Saturated vapour pressure of molten lead versus temperature

Figure 2.8.2. Deviation of the selected literature data on the saturated vapour pressure of lead from the recommended correlation (2.15)
It can be seen that the agreement in temperature dependence given by the different sources is satisfactory. However a significant scatter exists in values. Therefore Eq. (2.14) was chosen to construct an empirical correlation allowing one to calculate the vapour pressure of liquid bismuth as a function of temperature. Using the selected data, the following correlation was obtained for the saturated vapour pressure of molten bismuth where temperature is in kelvins:

$$p_{s,Bi}[Pa] = 2.4723 \times 10^{10} \cdot \exp\left(-\frac{22858}{T}\right)$$

(2.16)

This correlation is recommended for temperatures up to the normal boiling point.

The deviation of the selected literature data for the saturated vapour pressure of bismuth from the recommended correlation (2.16) is illustrated in Figure 2.8.4. One can see that very large differences exist between different sources. The recommended correlation (2.16) gives “the best estimate” with a maximum error of about 70%.

### 2.8.3 LBE

R.B. Tupper, et al. [Tupper, 1991] studied polonium evaporation from LBE and published some experimental results on the LBE (saturation) vapour pressure at temperatures 235-268 and 520-550°C (508-541, 793-823 K). Later Yu. Orlov, et al. [Orlov, 1997] published experimental values for the saturation pressure of the LBE vapour at equilibrium with the liquid phase at five different temperatures. However, both publications mentioned that a very large uncertainty in the pressure measurement exists at low temperatures (<500°C = 773 K). The results of [Orlov, 1997] were reproduced later in [Gromov, 1997]. New results have recently been communicated by P. Michelato, et al. [Michelato, 2003], P. Schuurmans, et al. [Schuurmans, 2005], and published by S. Ohno, et al. [Ohno 2005]. All these sources were included in the database and their results are plotted in Figure 2.8.5.
Figure 2.8.4. Deviation of the selected literature data on the saturated vapour pressure of bismuth from the recommended correlation (2.16)

Figure 2.8.5. Saturated vapour pressures of LBE versus temperature
Figure 2.8.5 illustrates that in the temperature range 650-1940 K, the vapour pressure of both lead and bismuth are very close to the experimental values for LBE available from [Tupper, 1991], [Orlov, 1997], [Schuurmans, 2005] and [Ohno, 2005]. The results of [Michelato, 2003] are systematically lower than the body of data, therefore they are not used. At temperatures of 500-550 K (227-277°C), Tupper, et al. [Tupper, 1991], and Orlov, et al. [Orlov, 1997], give a LBE vapour pressure that is an order of magnitude higher than the liquid-vapour equilibrium lines of lead and bismuth extrapolated to the lower temperatures. However, it should be noticed that at the expected level of saturated pressure (~10⁻⁸ Pa) it is very difficult to measure the pressure correctly, and overestimation by several orders of magnitude can often be obtained due to contamination of the liquid metal or of the experimental rig. Therefore it is proposed that these points not be considered at present.

The selected data set was used to determine the coefficients for a simplified equilibrium equation (2.14). The values of $\Delta H$ and $A$ thus obtained were: $\Delta H = 187.5$ kJ/mol and $A = 11.1 \cdot 10^9$ Pa. The obtained value of $\Delta H$ is in a good agreement with the value of the latent heat of LBE evaporation at the normal boiling point recommended in Section 2.7 (178 kJ/mol), taking into account the large uncertainty in the experimental results used for its calculation. The following simplified correlation for the saturation vapour pressure of molten LBE is recommended where temperature is in kelvins:

$$p_{\text{LBE}}[\text{Pa}] = 1.11 \cdot 10^{10} \cdot \exp\left(-\frac{22552}{T}\right)$$

(2.17)

This correlation similar to those proposed above for lead and bismuth. The deviation of the selected experimental values from this correlation is illustrated in Figure 2.8.6. The maximum deviation in the temperature range of 673-1943 K (400-1670°C) is about ±60%. (There is no agreement at all at the lower temperatures.) In spite of this significant deviation it was decided to not search for a more sophisticated formula given the very large dispersion of data obtained from different sources.

Figure 2.8.6. Deviation of the selected data on the saturated vapour pressures of LBE from the recommended Eq. (2.17)
2.9 Surface tension

A surface tension of liquid surfaces ($\sigma$) is related to tendency to minimise their surface energy. It decreases with temperature and reduces to zero at the critical temperature ($T_c$) where difference disappears between liquid and gas phases. According to Eötvös’ law [Imbeni, 1998a] for normal liquids this reduction can be described by formula:

$$\sigma = K_\sigma \cdot V_a^{2/3} \cdot (T_c - T)$$  \hspace{1cm} (2.18)

where $V_a$ is the molar volume. The average value of the coefficient $K_\sigma$ for normal liquid metals is $6.4 \cdot 10^{-8} \text{ J m}^{-2} \text{ K}^{-1} \text{ mol}^{-2/3}$.

B.J. Keene [Keene, 1993] reviewed many data on the surface tension of pure metals and also concluded that the temperature dependence of the surface tension is linear for most liquid metals:

$$\sigma = a + b \cdot T$$  \hspace{1cm} (2.19)

2.9.1 Lead

Based on the results of analysis of V. Imbeni, et al. [1998a] the following sources were included in the database for the surface tension of molten lead as a function of temperature: [Lyon, 1954], [Friedland, 1966], [Smithells, 1983, 2004], [Lucas, 1984], [Gmelins, 1986], [Jauch, 1986], [Iida, 1988], [Keene, 1993]. Moreover, later data of P.L. Kyrillov and G.P. Bogoslovskaia [Kyrillov, 2000a] and of the IAEA report [TECDOC-1289, 2002] were also included.


Figure 2.9.1 shows the values of surface tension of lead taken from the selected sources. Most sources report only empirical coefficients (except [Lyon, 1954], [Kyrillov, 2000a] and [TECDOC-1289, 2002]), with the experimental values being limited to the surface tension in the region of the melting point. A difference of $\pm 5\%$ exists between the surface tension values given by different sources at $T < 1000 \text{ K}$ (727°C). The lowest values are given by Friedland [Friedland, 1966] and the highest by Smithells [Smithells, 2004]. The values calculated using the correlation given in [Iida, 1988], [Lucas, 1984] and [Jauch, 1986] are very close in this temperature range. At higher temperatures, the scatter increases. The temperature slopes of the different correlations can be to up to $\pm 50\%$.

The correlation proposed by U. Jauch and B. Schultz [Jauch, 1986] allows a compromise represented by the following formula where temperature is in kelvins:

$$\sigma_{\text{JSH}} \left[ \text{N m}^{-1} \right] = 0.519 - 1.13 \cdot 10^{-4} \cdot T$$  \hspace{1cm} (2.20)
Unfortunately, the temperature of validity is not reported in the literature source. In light of this a conservative validity range of from the melting temperature of 600.6 K to 1200 K (327.6-927°C) is considered acceptable.

**Figure 2.9.1. Lead surface tension as a function of temperature**

![Figure 2.9.1. Lead surface tension as a function of temperature](image)

**2.9.2 Bismuth**

As in the case of lead, the results of analysis of V. Imbeni, et al. [1998a] were used as starting point. The data for bismuth surface tension as a function of temperature were taken from [Lyon, 1954], [Howe, 1961], [Friedland, 1966], the Smithells Metals Reference Book [Smithells, 2004], [Lucas, 1984], [Iida, 1988] and [Keene, 1993].

H.E. Howe [Howe, 1961] cited [Lyon, 1954, 1960] and [Smithells, 1955] as main source along with a few older complementary sources. In the last edition of the Smithells Metals Reference Book [Smithells, 2004] a linear correlation from the book of B.C. Allen [Allen, 1972] was reproduced (the same correlation was also reproduced by Iida [Iida, 1988]). Lucas [Lucas, 1984] used the correlation taken from G. Lang, et al. [Lang, 1977]. As with lead, B.J. Keene [Keene, 1993] recommended a linear correlation with the coefficients obtained from an analysis of many previous sources (however, in his final recommendation B.J. Keene based only on seven sources). Figure 2.9.2 shows the selected values of surface tension of the molten bismuth in the range of temperature.

The empirical correlations reported by the Smithells Metals Reference Book [Smithells, 1983] and by T. Iida and R.I.L. Guthrie [Iida, 1988] give practically the same values as those of Lyon [Lyon, 1954] and of Howe [Howe, 1961]. The correlation, reported by Lucas [Lucas, 1984] gives 2-3% lower values of the surface tension than other correlations. A good compromise is a correlation obtained by Keene [Keene, 1993] on the basis of all sources analysed by him:

\[
\sigma_{Bi}[N\,m^{-1}] = 0.4255 - 8.0 \cdot 10^{-5} \cdot I 
\]  

(2.21)

where temperature is in kelvins. The expected validity range is \(T_{\text{melt}}\) -1300 K (1027°C).
2.9.3 LBE

The sources of data for surface tension of the molten LBE, found in the open literature and included in the present database (Table 2.9.3), are from R.N. Lyon [Lyon, 1954], R.R. Miller [Miller, 1951], V.K. Semenchenko [Semenchenko, 1961], I.V. Kazakova, et al. [Kazakova, 1984], R. Novacovic, et al. [Novacovic, 2002], D. Giuranno, et al. [Giuranno, 2002], and F.C. Pastor Torres [Pastor Torres, 2003]. In the handbook of P.L. Kyrillov and G.P. Bogoslovskaya [Kyrillov, 2002a] incorrect data on the surface tension of molten LBE were given. These data have been corrected by Kyrillov later in [TECDOC-1289]. The last results were also included in the database.

R.R. Miller [Miller, 1951] presented LBE surface tension values at 200, 300 and 400°C. R.N. Lyon [Lyon, 1954] reported only two values: \( \sigma = 367 \text{ dynes cm}^{-1} \) at \( T = 800^\circ\text{C} \), and \( \sigma = 356 \text{ dynes cm}^{-1} \) at 1000°C. I.V. Kazakova, et al. [Kazakova, 1984] measured surface tension of Pb-Bi melts using the sessile-drop method at temperatures up to 800°C (1073 K). R. Novacovic, et al. [Novacovic, 2002] and Giuranno [Giuranno, 2002] also used the sessile-drop method to study a molten Pb-Bi alloy with almost eutectic composition (43.9 wt.% Pb) over the temperature range of 623-773 K (350-500°C). F.C. Pastor Torres [Pastor Torres, 2003] recently measured LBE surface tension with the pendent drop method in an inert atmosphere at temperatures from 423 to 573 K (150-300°C). However, the results obtained at \( T < 473 \text{ K} \) (200°C) were discarded because of difficulties related to oxidation. The data from the above cited sources are presented in Table 2.9.1 and Figure 2.9.3.

The deviations for the LBE surface tension data are shown in Figure 2.9.4. The LBE data can be described with an uncertainty of less than 3% by the following linear correlation:

\[
\sigma_{LBE}[N\text{ m}^{-1}] = 0.437 - 6.6 \cdot 10^{-4} \cdot T
\]  \hspace{1cm} (2.22)

where temperature is in kelvins. The above correlation is recommended for estimation of the surface tension of molten LBE at normal pressure up to 1400 K (1127°C).
Table 2.9.1. LBE surface tension database

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.3.1</td>
<td>Surface tension</td>
<td>?</td>
<td>?</td>
<td>1073, 1273</td>
<td>~ 10^5 (?)</td>
<td>[Lyon, 1954]</td>
<td></td>
</tr>
</tbody>
</table>
| Interpolation function: $\sigma = (426.02 - 0.055 \cdot T \cdot 10^{-3}) \text{Nm}^{-1}$

Comments:                      |
| 9.3.2   | Surface tension | Sessile drop       | ?                  | 623-773              | ~ 10^5 (?)        | [Novacovic, 2002] |
| Interpolation function: $\sigma = (445.419 - 0.0801 \cdot T \cdot 10^{-3}) \text{Nm}^{-1}$

Comments: 43.9 wt.% Pb + 56.1 wt.% Bi. Unknown purity.          |
| 9.3.3   | Surface tension | Pendent drop       | ?                  | 423-573              | ~ 10^5 (?)        | [Pastor Torres, 2003] |
| Interpolation function: $\sigma = (450.86 - 0.0873 \cdot T \cdot 10^{-3}) \text{Nm}^{-1}$

Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity. |
| 9.3.4   | Surface tension | ?                  | ?                  | 1073-1373            | ~ 10^5 (?)        | [Semenchenko, 1961] |
| Interpolation function: $\sigma = (421.26 - 0.0665 \cdot T \cdot 10^{-5}) \text{Nm}^{-1}$

Comments:                      |
| 9.3.5   | Surface tension | ?                  | ?                  | 473-673              | ~ 10^5 (?)        | [Miller, 1951]   |
| Interpolation function: $\sigma = (421.26 - 0.0665 \cdot T \cdot 10^{-5}) \text{Nm}^{-1}$

Comments:                      |
| 9.3.6   | Surface tension | Sessile drop       | ?                  | ??-??-1073           | ~ 10^5 (?)        | [Kazakova, 1984] |
| Interpolation function: $\sigma = (415.7 - 0.047 \cdot T \cdot 10^{-3}) \text{Nm}^{-1}$

Comments: 43.3 wt.% Pb + 56.7 wt.% Bi. Unknown purity.          |
| 9.3.7   | Surface tension | ?                  | ?                  | 403-1073             | ~ 10^5 (?)        | [TECDOC-1289, 2002] |
| Interpolation function: $\sigma = (444.0 - 0.0703 \cdot T \cdot 10^{-3}) \text{Nm}^{-1}$

Comments: 44.5 wt.% Pb + 55.5 wt.% Bi.                      |
Figure 2.9.3. Surface tension of the molten LBE

![Surface tension of the molten LBE](chart1.png)

Figure 2.9.4. Deviation of the source data on surface tension of molten LBE from the recommended correlation (2.21)

![Deviation of the source data on surface tension](chart2.png)
2.10 Density

The temperature dependence of density provides essential information for the development of an equation of state (EOS). In engineering practice it is used to determine the concentration of atoms in unit volume and hydraulic parameters in installations. Also, the measurement or calculation of basic physical properties, e.g. viscosity, surface tension, thermal diffusivity, requires knowledge of density.

2.10.1 Lead


The recommendations of Friedland [Friedland, 1966] and Weeks [Weeks, 1971] have not been taken into account because they repeat the results of [Smithells, 1955] and [Lyon, 1954] already included in the database.

The selected database for density of molten lead is presented in Table 2.10.1.

Figure 2.10.1 shows the molten lead density values from the selected sources versus temperature.

A set of the selected data can be described by linear temperature dependence where temperature is in kelvins:

$$ \rho_{\text{Pb}} [\text{kg m}^{-3}] = 11367 - 1.1944 \cdot T $$

(2.23)

The deviation of the selected source values from Eq. (2.23) is illustrated in Figure 2.10.2. One can see that maximum difference does not exceed 0.7%.

Table 2.10.1. Database on the density of molten lead at the normal pressure

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Interpolation function: $\rho = 11291 - 1.165 \cdot T$ kg m^{-3}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.1.2</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>673-1073</td>
<td>~ 10^5 (?)</td>
<td></td>
<td>[Kutateladze, 1959]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: $\rho = 11380 - 1.169 \cdot T$ kg m^{-3}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.10.1. Database on the density of molten lead at the normal pressure (cont.)

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1.3</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>601-1345</td>
<td>~ 10^5 (?)</td>
<td>[Crean, 1964]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.1.4</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>601-1823</td>
<td>~ 10^5 (?)</td>
<td>[Smithells, 1983]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.1.6</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>603-1273</td>
<td>~ 10^5 (?)</td>
<td>[TECDOC-1289, 2002]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.1.7</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>636-829</td>
<td>~ 10^5 (?)</td>
<td>[Ruppersber, 1976]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comments: Unknown purity.

Interpolation function:

\[
\rho = 11307 - 1.177 \cdot T \text{ kg m}^{-3}
\]

Interpolation function:

\[
\rho = 11418 - 1.301 \cdot T + 6.278 \cdot 10^{-5} \cdot T^2 \text{ kg m}^{-3}
\]

Interpolation function:

\[
\rho = 10670 - 1.32 \cdot (T - T_{melt}) \text{ kg m}^{-3}
\]

Interpolation function:

\[
\rho = 11417 - 1.239 \cdot T \text{ kg m}^{-3}
\]

Interpolation function:

\[
\rho = 11417 - 1.350 \cdot T \text{ kg m}^{-3}
\]

Comments: Unknown purity.

Figure 2.10.1. Density of molten lead as function of temperature at normal pressure
2.10.2 Bismuth

The data for molten bismuth density that have been included in the database, were taken from [Lyon, 1954], [Kutateladze, 1959], [Crean, 1964], [Cahil, 1963], [Bonilla, 1964], [Lucas, 1984] and [Iida, 1988].

Data from Smithells Metal Reference Book [Smithells, 1983], Friedland [Friedland, 1966] and Weeks [Weeks, 1971] have not been included in the database because they reproduce the results already presented in the above cited sources. Bonilla [Bonilla, 1964] reported values that were obtained by interpolation of data collected from a number of sources. Iida and Guthrie [Iida, 1988] reproduce the recommendations of Steinberg [Steinberg, 1974].

The selected database on the density for molten bismuth is presented in Table 2.10.2.

Figure 2.10.3 shows the molten bismuth density values from the selected sources versus temperature.

All sets of the selected data can be described with linear temperature dependence recommended by V. Imbeni, et al. [Imbeni, 1998a]:

\[
\rho_{\text{Bi}} \left[ \text{kg m}^{-3} \right] = 10726 - 1.2208 \cdot T
\]  

(2.24)

where temperature is in kelvins.

The deviation of the selected source values from Eq. (2.24) is illustrated in Figure 2.10.4. One can see that maximum difference does not exceed 0.4%.
### Table 2.10.2. Database on the density of the molten bismuth at the normal pressure

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Pressure range, Pa</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.2.1</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>573-1235</td>
<td>~ 10^5 (?)</td>
<td>[Lyon, 1954]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $\rho = 10755 - 1.258 \cdot T \text{ kg m}^{-3}$</td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.2.2</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>553-973</td>
<td>~ 10^5 (?)</td>
<td>[Kutateladze, 1959]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $\rho = 10744 - 1.243 \cdot T \text{ kg m}^{-3}$</td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.2.3</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>589-1033</td>
<td>~ 10^5 (?)</td>
<td>[Bonilla, 1964]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $\rho = 10722 - 1.211 \cdot T \text{ kg m}^{-3}$</td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.2.4</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>566-1266</td>
<td>~ 10^5 (?)</td>
<td>[Crean, 1964]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $\rho = 10700 - 1.3174 \cdot T \text{ kg m}^{-3}$</td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.2.5</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>673-1273</td>
<td>~ 10^5 (?)</td>
<td>[Lucas, 1984]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $\rho = 10714 - 1.1986 \cdot T \text{ kg m}^{-3}$</td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.2.6</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>601-2000</td>
<td>~ 10^5 (?)</td>
<td>[Iida, 1988]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $\rho = 10050 - 1.18 \cdot (T - T_{\text{melt}}) \text{ kg m}^{-3}$</td>
<td></td>
<td>Comments: Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 2.10.3. Density of molten bismuth as a function of temperature at normal pressure**
2.10.3 LBE

Only data that do not repeat one another have been included in the database for molten LBE presented in Table 2.10.3. The data included are from R.N. Lyon [Lyon, 1954], S.S. Kutateladze [Kutateladze, 1959], the IAEA report [TECDOC-1289, 2002] and B.B. Alchagirov [Alchagirov, 2003].

The data presented by C.F. Bonilla [Bonilla, 1964], Crean [Crean, 1964] and Hofman [Hofmann, 1970] were obtained by the interpolation of the results of Lyon [Lyon, 1954, 1956] and were therefore not included in the database.

The extracted density values as a function of temperature at normal atmospheric pressure are presented in Figure 2.10.5. The temperature dependence of the densities of pure molten lead and pure molten bismuth, calculated with the empirical correlations recommended in preceding sections are also reproduced for comparison.

The linear regression of values presented in Figure 2.10.5 yields for the LBE density:

$$\rho_{\text{LBE}} \left[ \text{kg m}^{-3} \right] = 11096 - 1.3236 \cdot T$$

where the temperature is in kelvins.

Figure 2.10.6 shows that the deviation of the selected literature data for molten LBE density from Eq. (2.25) does not exceed 0.8%.
### Table 2.10.3. LBE density database

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.3.1</td>
<td>Density</td>
<td>?</td>
<td>?</td>
<td>473-1273</td>
<td>~ 10^5 (?)</td>
<td>[Lyon, 1954]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.3.2</td>
<td>Density</td>
<td>Picnometer</td>
<td>2%</td>
<td>403-973</td>
<td>~ 10^5 (?)</td>
<td>[Kutateladze, 1959]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.3.3</td>
<td>Density</td>
<td>Picnometer</td>
<td>?</td>
<td>403-1073</td>
<td>~ 10^5 (?)</td>
<td>[TECDOC-1289, 2002]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.3.4</td>
<td>Density</td>
<td>Picnometer</td>
<td>0.1%</td>
<td>410-726</td>
<td>~ 10^5 (?)</td>
<td>[Alchagirov, 2003]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Interpolation function:**

- For 10.3.1: \( \rho = 11113 - 1.375 \cdot T \) kg m\(^{-3}\)
- For 10.3.2: \( \rho = 11062 - 1.2175 \cdot T \) kg m\(^{-3}\)
- For 10.3.3: \( \rho = 11047 - 1.2564 \cdot T \) kg m\(^{-3}\)
- For 10.3.4: \( \rho = 10981.7 - 1.1369 \cdot T \) kg m\(^{-3}\)

**Comments:**

- 10.3.1: Unknown data on eutectic composition and purity.
- 10.3.2: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.
- 10.3.3: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.
- 10.3.4: 44.6 wt.% Pb + 55.4 wt.% Bi. Purity Pb – 99.9985 wt.%. Purity Bi – 99.98 wt.%

---

**Figure 2.10.5. Density of the melted LBE versus temperature**

![Graph showing density of LBE, Pb, and Bi as a function of temperature.](image)
In Figures 2.10.5 and 2.10.6, the results of calculation of the LBE density using Vegard’s law which expresses the molar volume of LBE through the molar fractions \( x_{\mu_{\text{Pb}}} \) and \( x_{\mu_{\text{Bi}}} \) and the molar volumes \( v_{\mu_{\text{Pb}}} \) and \( v_{\mu_{\text{Bi}}} \) of lead and bismuth as follows:

\[
v_{\mu_{\text{LBE}}} = x_{\mu_{\text{Pb}}} \cdot v_{\mu_{\text{Pb}}} + x_{\mu_{\text{Bi}}} \cdot v_{\mu_{\text{Bi}}}
\]  

are also presented.

Eq. (2.26), transformed to the following form:

\[
\rho_{\text{LBE}} = \frac{x_{\mu_{\text{Pb}}} \cdot \mu_{\text{LBE}}}{\rho_{\text{Pb}}} + \frac{(1-x_{\mu_{\text{Pb}}}) \cdot \mu_{\text{Bi}}}{\rho_{\text{Bi}}}
\]  

(2.27)

(where \( \mu_{\text{Pb}} \), \( \mu_{\text{Bi}} \) and \( \mu_{\text{LBE}} \) are the molar masses of Pb, Bi and LBE respectively) allows one to calculate the LBE density using as input the densities of pure molten lead and pure molten bismuth which can be predicted with better precision than that of LBE.

From Figures 2.10.5 and 2.10.6 one can see that the Vegard’s law can be used for calculation of the LBE density as a good approximation. In spite the fact that the Vegard’s law can not be applied to LBE at temperatures lower than highest melting point of the component, it gives very good results from the LBE melting temperature to at least 1300 K (1027°C) if one extrapolates the correlations for the densities of the melted Pb and Bi down to \( T_{\text{melt, LBE}} \).

### 2.11 Thermal expansion

The density of liquid metals changes with temperature due to thermal expansion related to anharmonicity of interatomic forces. In a general case, a link between the density and the coefficient
of volumetric thermal expansion at any constant thermodynamic parameter \( x \) is defined by the following formula:

\[
\beta_x(T) = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_x = - \frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_x
\]  

(2.28)

Literature sources describing a direct measurement of the coefficient of thermal expansion (CTE) of molten Pb, Bi and LBE were not found. Therefore, available information on the temperature dependence of their density (see Section 2.10) was used for deduction of the isobaric CTE. Substituting the correlation for density recommended in Section 2.10 into definition (2.28) yields the following formulae for the isobaric volumetric CTE of molten lead, bismuth and LBE respectively:

a) Lead:

\[
\beta_{Pb} [K^{-1}] = \frac{1}{9516.9 - T}
\]  

(2.29)

b) Bismuth:

\[
\beta_{Bi} [K^{-1}] = \frac{1}{8786.2 - T}
\]  

(2.30)

c) LBE:

\[
\beta_{LBE} [K^{-1}] = \frac{1}{8383.2 - T}
\]  

(2.31)

The results obtained are presented in Figure 2.11.1. Comparison of the isobaric volumetric CTE of molten lead, bismuth and LBE, obtained with the formulae above shows that LBE has the highest CTE. In principle, this can be explained by the lower attractive forces between Pb and Bi atoms in LBE than in pure lead and in pure bismuth. However, it could also be due to a large uncertainty of the determination of the thermal expansion coefficient by using the procedure of differentiation of the density correlations.

Eqs. (2.29), (2.30) and (2.31) are recommended for practical applications as “the best choice” (because of their consistency with the correlations recommended above in Section 2.10) for calculation of the CTE of molten lead, bismuth and LBE respectively.

2.12 Sound velocity and compressibility

There are no results for direct measurement of the compressibility for molten lead, bismuth and LBE in the literature. Usually, the adiabatic compressibility \( K_S \) (or the adiabatic elastic modulus \( B_S \)) is found from the results of measurement of the sound velocity \( u_{sound} \) and density \( \rho \) using the following thermodynamic relationship [Dreyfus, 1971]:

\[
B_S = -V \left( \frac{\partial \rho}{\partial V} \right)_S = \frac{1}{K_S} = \frac{\rho}{\left( \frac{\partial \rho}{\partial \rho} \right)_S} = \rho \cdot u_{sound}^2
\]  

(2.32)
2.12.1 Lead

The velocity of propagation of longitudinal sound waves in molten lead was measured by O.J. Kleppa [Kleppa, 1950] close to the melting point, by R.B. Gordon [Gordon, 1959] over a temperature interval from the melting temperature to 643 K (370°C), by G.M. Mustafin and G.F. Shailhiev [Mustafin, 1983] over the temperature range 601-2000 K and by G.V. Konyuchenko [Konyuchenko, 1969] over the temperature range 673-973 K (400-700°C). Rather good agreement is observed among the first three sources in the region of the melting temperature. The sound velocity values presented by Konyuchenko [Konyuchenko, 1969] are 3% higher. No information was given on Pb purity and on the measurement method used. Therefore this source was not taken into account in the database presented in Table 2.12.1 below. The data are plotted in Figure 2.12.1.

The most complete and reliable data seems to be that from Mustafin and [Mustafin, 1983], therefore the correlation recommended for the estimation of the sound velocity in the molten lead is:

\[
u_{\text{sound, Pb}} \left[ \text{m s}^{-1} \right] = 1951.75 - 0.3423 \cdot T + 7.635 \cdot 10^{-5} \cdot T^2 \]  

(2.33)

where temperature is in kelvins.

2.12.2 Bismuth

The sound velocity in molten bismuth was measured by J. Jarzynski [Jarzynski, 1963] from the melting temperature up to 603 K (330°C). This work has been included in the database shown in Table 2.12.2.
Table 2.12.1. Sound velocity in the molten lead

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy %</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.1.1</td>
<td>Sound velocity</td>
<td>Pulse propagation</td>
<td>0.01</td>
<td>601-643</td>
<td>~ 10^5 (2)</td>
<td>[Gordon, 1959]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.1.2</td>
<td>Sound velocity</td>
<td>Pulse propagation</td>
<td>0.005</td>
<td>601-2000</td>
<td>~ 10^5 (2)</td>
<td>[Mustafin, 1983]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.1.3</td>
<td>Sound velocity</td>
<td>?</td>
<td></td>
<td>600.2</td>
<td>~ 10^5 (2)</td>
<td>1790 m/s</td>
<td>[Kleppa, 1950]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Interpolation function: \( u_{\text{sound}}(T) = 1776-0.277(T - T_{\text{melt}}) \) m s^{-1}
Comments: Lead of technical purity.

Interpolation function: \( u_{\text{sound}}(T) = 1951.75-0.3423\cdot T + 7.635\cdot 10^{-5} \cdot T^2 \) m s^{-1}
Comments: Pure lead.

Interpolation function: n/a
Comments: Unknown purity.

Figure 2.12.1. Velocity of ultrasound in the molten lead in function of temperature

![Graph showing the velocity of ultrasound in the molten lead vs temperature](image)

Table 2.12.2. Sound velocity in the molten bismuth

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy %</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.2.1</td>
<td>Sound velocity</td>
<td>Pulse propagation</td>
<td>?</td>
<td>545-603</td>
<td>~ 10^5 (2)</td>
<td>[Jarzynski, 1963]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Interpolation function: \( u_{\text{sound}} = 2111.3 - 0.7971\cdot T \) m s^{-1}
Comments: Lead of technical purity.
In the publication of Jarzynski [Jarzynski, 1969] it was proposed that the temperature dependence of the sound velocity in molten bismuth followed a linear correlation:

\[ u_{\text{sound Bi}} \left[ \text{m s}^{-1} \right] = 2111.3 - 0.7971 \cdot T \]  

(2.34)

where temperature is in kelvins.

### 2.12.3 LBE

The ultrasound velocity in molten LBE has been measured by R. Kažys [Kažys, 2002] over the temperature range 433-603 K (160-330°C). The results of this publication have been included in the database in Table 2.12.3. A-M. Azad [Azad, 2005] calculated the sound velocity in molten LBE based on Vegard’s law and using the experimental data on the sound velocity in lead [Mustafin, 1969] and in bismuth [Jarzynski, 1963]. The correlation recommended by Azad [Azad, 2005] has also been included in the database.

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy %</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.3.1</td>
<td>Sound velocity</td>
<td>Direct propagation</td>
<td>0.1</td>
<td>433-603</td>
<td>~ 10^5 (?)</td>
<td></td>
<td>[Kažys, 2002]</td>
</tr>
</tbody>
</table>
|          | Interpolation function: \( u_{\text{sound LBE}}(T) = 1773 + 0.1049 \cdot T - 2.873 \cdot 10^{-4} \cdot T^2 \) m s\(^{-1}\)  
|          | Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity. |
| 12.3.2   | Sound velocity     | –                  | ?                    | ~ 10^5 (?)          |                   |             | [Azad, 2005] |
|          | Interpolation function: \( u_{\text{sound LBE}}(T) = 2041.58 - 0.5987 \cdot T + 3.3387 \cdot 10^{-5} \cdot T^2 \) m s\(^{-1}\)  
|          | Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity. |

The values for the sound velocity in LBE are plotted in Figure 2.12.2 together with plots for the recommended correlations for lead and bismuth.

The Vegard’s law points are extrapolated to the melting temperature of LBE. From Figure 2.12.2 one can see that difference between the experimental data on the sound velocity and those obtained with the Vegard’s law is less then 2% in the region of the melting temperature of lead. However, the slope of the temperature dependence differs significantly (more than twice).

While the present data is very scattered and, the following correlation for the LBE sound velocity is based on the experimental results of Kazys [Kazys, 2002]:

\[ u_{\text{sound LBE}} \left[ \text{m s}^{-1} \right] = 1773 + 0.1049 \cdot T - 2.873 \cdot 10^{-4} \cdot T^2 \]  

(2.35)

where temperature is in kelvins.
Figure 2.12.2. Sound velocity in molten LBE, Pb and Bi versus temperature

The results of the calculations for elastic modulus of molten lead, bismuth and LBE obtained with Eq. (2.32) are presented in Figure 2.12.3.

In the respective temperature range and at normal atmospheric pressure, the temperature dependence of the elastic modulus can be described with the help of parabolic and linear functions.

a) Lead:

\[ B_{s,Pb}[Pa] = \left( 42.15 - 1.652 \cdot 10^{-2} \cdot T + 3.273 \cdot 10^{-6} \cdot T^2 \right) \cdot 10^9 \]  

(2.36)

b) Bismuth:

\[ B_{s,Bi}[Pa] = \left( 44.67 - 0.0299 \cdot T \right) \cdot 10^9 \]  

(2.37)

c) LBE:

\[ B_{s,LBE}[Pa] = \left( 35.18 - 1.541 \cdot 10^{-3} \cdot T - 9.191 \cdot 10^{-6} \cdot T^2 \right) \cdot 10^9 \]  

(2.38)

where temperatures are in kelvins.

2.13 Heat capacity

Available experimental data on heat capacity of heavy liquid metals are even less numerous than those for density. The theoretical calculation of heat capacity of liquids is restricted by the extreme complexity of the motion of atoms in liquids. Often, the same types of empirical correlations as for solids are used to fit the experimental results. An extensive review of the existing experimental data on the heat capacity of lead, bismuth and LBE was performed by V. Imbeni, et al. [Imbeni, 1998a, 1998b].
Figure 2.12.3. Bulk elastic modulus of molten LBE versus temperature

![Graph showing elastic modulus vs. temperature for LBE, Bi, and Pb](Image)

2.13.1 Lead

The heat capacity data of lead taken from [Lyon, 1954], [Kutateladze, 1959], [Friedland, 1966], [Hultgren, 1974], [Kubaschewski, 1979, 1993], [Iida, 1988] and [Gurvich, 1991] have been analysed to include in the current database.


Data presented in [Kyrillov, 200b] and [TECDOC-1289, 2002] repeat those of [Kutateladze, 1959], therefore they were not included in the database.

Figure 2.13.1 shows the values of heat capacity taken from the selected literature for lead.

R.N. Lyon [Lyon, 1954] gives higher values for the heat capacity of lead than those reported by other sources. The values recommended by S.S. Kutateladze [Kutateladze, 1959] are independent of temperature. At temperatures higher than 1300 K (1027°C) two tendencies are observed. According to Friedland [Friedland, 1966], Iida and Guthrie [Iida, 1988], the specific heat of lead decreases linearly with temperature, while according to R. Hultgren, et al. [Hultgren, 1974] it remains constant.
A reasonable choice for the heat capacity of molten lead in the temperature range of $T_{\text{melt}}$ to 1300 K (1027°C) is the recommendation of [Gurvich, 1991] where temperature is in kelvins:

$$
\begin{align*}
    c_p \text{Pb} &\left(\frac{J}{kg \cdot K}\right) = 175.1 - 4.961 \times 10^{-2} \cdot T + 1.985 \times 10^{-5} \cdot T^2 - 2.099 \times 10^{-9} \cdot T^3 - 1.524 \times 10^6 \cdot T^{-2} \\
\end{align*}
$$

(2.39)

2.13.2 Bismuth

The data for the heat capacity of bismuth as a function of temperature analysed in this handbook have been taken from [Lyon, 1954], [Kutateladze, 1959], [Hultgren, 1974], [Iida, 1988], [Kubaschewski, 1993], [Cheynet, 1996] and Smithells Metal Reference Book [Smithells, 2004]. Howe [Howe, 1961] and Crean [Crean, 1964] reported values given earlier by Lyon [Lyon, 1954, 1960], and were not included in the database.

Figure 2.13.2 shows the values of heat capacity for molten bismuth extracted from the selected literature sources in the temperature range of interest. As it can be seen, the values reported by R.N. Lyon [Lyon, 1954] increase with temperature and those of S.S. Kutateladze [Kutateladze, 1959] remain constant, in contrast with the results published by other authors. These data were not used in the development of the recommended correlation.

Basing on analogy with other liquid metals the data were chosen with the heat capacity values decreasing with temperature, and the correlation proposed by V. Imbeni, et al. [Imbeni 1998a] (transformed to other units) is recommended to use for the isobaric specific heat of molten bismuth:

\[ c_{p,\text{Bi}} = 118.2 + 5.934 \times 10^{-3} \cdot T + 71.83 \times 10^3 \cdot T^{-2} \]  

Eq. (2.40) is applicable in the temperature range of \( T_{\text{melt}} \) to 1300 K (1027°C).

2.13.3 LBE

Available data on the heat capacity of LBE are very limited. The authors have found only three independent sources where heat capacity of molten LBE is given at different temperatures: [Lyon, 1954], [Kutateladze, 1959], and [Hultgren, 1973]. The two older publications, [Lyon, 1954] and [Kutateladze, 1959], recommend the same value of \( c_{p,\text{LBE}} = 0.035 \) cal g\(^{-1}\) °C\(^{-1}\) for a range of temperatures. In Chapter 2 of the original handbook of Lyon [Lyon, 1954] it was only indicated that this value has been obtained in the temperature interval from 144 to 358°C. However, in Chapter 5 of the same handbook this value was presented as interpolation for the interval of 300 to 700°F (149-371°C or 422-644 K). In [Kutateladze, 1959] this value was recommended for temperatures from 130°C to 700°C (403-973 K). This recommendation was reproduced in later handbooks [Mantell, 1958], [Lyon, 1960], [Bonilla, 1964], [Crean, 1964], [Friedland, 1966], and some of them even extended it to higher
temperatures without any explanation. This value (but in SI units – 146 J kg$^{-1}$ K$^{-1}$) was recently repeated in [Kyrillov, 2000a] and then reproduced in [TECDOC-1289, 2002]. The only source which reports the LBE heat capacity as a function of temperature is that of R. Hultgren, et al. [Hultgren, 1973], which refers to a report of T.B. Douglas and J.L. Dever [Douglas, 1953] as the original source. The data from [Hultgren, 1973] were reprinted in later compilations and a linear interpolation was proposed in [Imbeni, 1998b] and in [Morita, 2004]. Based on an analysis of the available data, the information from three sources: [Lyon, 1954], [Kutateladze, 1959], and [Hultgren, 1973] is included in the database shown in Table 2.13.1. Figure 2.13.3 shows plots of the heat capacity of molten LBE as a function of temperature.

### Table 2.13.1. Heat capacity database of LBE

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy %</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $c_p^{LBE}(T) = 146.5$ J kg$^{-1}$ K$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.1.2</td>
<td>Specific heat</td>
<td>Direct heating</td>
<td>?</td>
<td>403-973</td>
<td>~ 10$^5$ (?)</td>
<td>Annex</td>
<td>[Kutateladze, 1959]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $c_p^{LBE}(T) = 146.5$ J kg$^{-1}$ K$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.1.3</td>
<td>Specific heat</td>
<td>Heat evolution</td>
<td>5 %</td>
<td>400-1100</td>
<td>~ 10$^5$ (?)</td>
<td>Annex</td>
<td>[Hultgren, 1973]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Interpolation function: $c_p^{LBE}(T) = 160 - 0.0239$ T J kg$^{-1}$ K$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Comments: 45.3 wt.% Pb + 54.7 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 2.13.3. Specific heat of molten LBE versus temperature**

![Figure 2.13.3. Specific heat of molten LBE versus temperature](image-url)
A line obtained with the additive Kopp’s law (often used for calculation of the heat capacities of the binary systems) is as follows:

\[ c_{p_{LBE}} = \frac{x_{Pb} \cdot \mu_{Pb} \cdot c_{Ppb} + (1 - x_{Pb}) \cdot \mu_{Bi} \cdot c_{Pb}}{\mu_{LBE}} \]  

(2.41)

where \( c_{p_{Pb}} \) and \( c_{p_{Bi}} \) are the specific heat capacities, \( x_{Pb} \) and \( x_{Bi} \) are the weight contents and \( \mu_{Pb} \) and \( \mu_{Bi} \) are molecular masses of lead and bismuth in LBE.

In spite of a good agreement between the values of the selected sources and with the Kopp’s law in the temperature interval between the melting temperatures of lead and bismuth 267-327°C (540-600 K), a disagreement exists in the temperature dependence, leading to a larger difference at higher temperatures.

Attempting, on the one hand, to take into account the similarity between LBE and its components (Pb and LB) and, on other hand, to use the available experimental data on LBE specific heat, a fitting of the data set was developed using values given above with a parabolic polynomial (also taking into account the values obtained with the Kopp’s law) in the temperature range of 400-1100 K (127-827°C) with the results as follows:

\[ c_{p_{LBE}} \left[ J \cdot kg^{-1} \cdot K^{-1} \right] = 159 - 2.72 \cdot 10^{-2} \cdot T + 7.12 \cdot 10^{-6} \cdot T^2 \]  

(2.42)

where temperature is in kelvins.

The deviation of the data included in the data set from the recommended Eq. (2.42) is illustrated by Figure 2.13.4.

**Figure 2.13.4. Deviation of the available data on heat capacity of molten LBE from Eq. (2.42)**
From Figure 2.13.4 one can see that the deviation of the selected values of the LBE specific heats from the recommended Eq. (2.42) does not exceed 5% in the temperature range of 400-1100 K (127-827°C). The deviation is about the same using Kopp’s law.

2.14 Critical constants and equation of state

2.14.1 Critical parameters

2.14.1.1 Lead

G. Pottlacher [Pottlacher, 1990] published a summary of experimentally determined and theoretically estimated parameters for the critical point of lead available in the literature as of this date. They considered 16 sets of data as well as their own estimations based on experimental results obtained using the pulse-heating technique. Their summary shows that the experimental and theoretical data on the critical temperature of lead (T_c Pb) lie within the range of 3584-6000 K (3311-5727°C), while their own estimation yields T_c Pb = 5400 ± 400 K (5127 ± 400°C).

M.M. Martynyuk [Martynyuk, 1998] estimated the critical points of metals by determining parameters of the generalised Van der Waals (VdW) equation using experimental data on liquid phase density and heat of vaporisation in the temperature range from the triple point to the normal boiling point. The calculated results for lead were compared with the experimental data obtained by himself [Martynyuk, 1983]. Poor agreement between the theoretical and experimental values on the critical pressure and density was explained by low accuracy (~50%) in the experiment. Values of T_c Pb = 4766 K (4493°C), p_c Pb = 90 MPa, \( \rho_c Pb = 2259 \text{ kg/m}^3 \) were recommended for the critical point of lead.

K.M. Watson [Watson, 1933] proposed a theoretical method for estimating the critical temperature of non-polar or a slightly polar material and deduced the following formula:

\[
\frac{T_c}{T_b} = 0.283 \left( \frac{M}{\rho_l(T_b)} \right)^{0.18}
\]

where M is in g/mol, \( \rho_l(T_b) \) is the liquid density in g/cm\(^3\) at the normal boiling point T_b and T_c is the temperature at which the molar volume of vapour is 22.4·10\(^{-3}\) m\(^3\)/mol. The following relation was used to calculate T_c based on the work of T.C. Chawla, et al. [Chawla, 1981]:

\[
\ln T_c = \frac{9.8 T_e}{T_b} - 4.2
\]

The critical density can be estimated from the semi-empirical “law of rectilinear diameter” [Cailletet, 1986]. With a reported value for the critical compressibility, Z_c, of 0.21 for lead [Pottlacher, 1998] the following values were obtained: T_c Pb = 4961 K, p_c Pb = 114 MPa and \( \rho_c Pb = 2720 \text{ kg/m}^3 \).

Recently, A-M. Azad [Azad, 2005] estimated the critical temperatures of lead, bismuth and LBE with a theoretical model called “the internal pressure approach”, which is described below in Section 2.14.1.3. The estimation for lead indicates a quite low value of the lead critical temperature (T_c Pb = 3096-3118°C (3369-3391 K)) in comparison with most of other reported theoretical and experimental values. This can be explained by errors in extrapolation of the experimental data to the high temperatures.
A summary of data on the critical point of lead extracted from the above-cited literature is presented in Table 2.14.1 (the data reviewed in [Pottlacher, 1990] are not included – only their recommendation is reproduced in the table). The critical compressibility, $Z_c$, is determined in the table as follows:

$$Z_c \equiv \frac{p_c V_c}{RT_c} = \frac{p_c M}{RT_c \rho_c}$$  \hfill (2.45)$$

where $M$ is the molecular mass and $R = 8.314 \text{ J/mol}$ is the universal gas constant.

### Table 2.14.1. Summary of the critical point data for lead

<table>
<thead>
<tr>
<th>Reference</th>
<th>$T_c$ [K]</th>
<th>$p_c$ [MPa]</th>
<th>$\rho_c$ [kg/m$^3$]</th>
<th>$Z_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Martynyuk, 1983]</td>
<td>4460</td>
<td>160</td>
<td>2950</td>
<td>0.30</td>
</tr>
<tr>
<td>[Pottlacher, 1990]</td>
<td>5400 ± 400</td>
<td>250 ± 30</td>
<td>3200 ± 300</td>
<td>0.36</td>
</tr>
<tr>
<td>[Martynyuk, 1998]</td>
<td>4776</td>
<td>90</td>
<td>2259</td>
<td>0.21</td>
</tr>
<tr>
<td>[Pottlacher, 1998]</td>
<td>4961</td>
<td>114</td>
<td>2720</td>
<td>0.21</td>
</tr>
<tr>
<td>[Azad, 2005]</td>
<td>3369-3391</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

From Table 2.14.1 one can see that the later more accurate results of M.M. Martinuk [Martynyuk, 1998] and G. Pottlacher [Pottlacher, 1998] are in a very good agreement. Taking into account a large uncertainty in the estimations, the mean rounded values of these two sources are recommended for the critical temperature, pressure and density of lead:

$$T_{c, \text{Pb}} = 4870 \text{ K (4597°C)}, \quad p_{c, \text{Pb}} = 100 \text{ MPa}, \quad \rho_{c, \text{Pb}} = 2490 \text{ kg/m}^3$$  \hfill (2.46)$$

### 2.14.1.2 Bismuth

Only a few sets of the critical point data are available for bismuth. A.V. Grosse [Grosse, 1961] estimated the critical temperature of bismuth ($T_{c, \text{Bi}} = 4620 \text{ K (4347°C)}$) by application of the principle of corresponding states to the enthalpy of vaporisation. J.A. Cahill, et al. [Cahill, 1968] compared this value with one estimated by the method of rectilinear diameter ($T_{c, \text{Bi}} \approx 5000 \text{ K (4727°C)}$), which assumes that the average density of the liquid and the saturated vapor changes linearly with temperature. V.E. Fortov, et al. [Fortov, 1975] calculated the theoretical values of the critical temperature ($T_{c, \text{Bi}} = 4200 \text{ K (3927°C)}$), pressure ($p_{c, \text{Bi}} = 126 \text{ MPa}$) and density ($\rho_{c, \text{Bi}} = 2660 \text{ kg/m}^3$) of bismuth, based on traditional approaches such as the Grosse method [Grosse, 1961] and on the method of rectilinear diameter [Pottlacher, 1998]. Martynyuk [Martynyuk, 1983] estimated the parameters of the critical point of bismuth from the pulse heating experiment and obtained $T_{c, \text{Bi}} = 3780 \text{ K (3507°C)}$, $p_{c, \text{Bi}} = 132 \text{ MPa}$ and $\rho_{c, \text{Bi}} = 3010 \text{ kg/m}^3$. The estimation of the critical parameters using the Watson method [Watson, 1931] and the law of rectilinear diameter yields: $T_{c, \text{Bi}} = 4354 \text{ K (4081°C)}$ and $p_{c, \text{Bi}} = 2705 \text{ kg/m}^3$. The critical temperature of bismuth estimated by Azad [Azad, 2005] ($T_{c, \text{Bi}} = 2042-2106 \text{ K (1769-1883°C)}$) is lower than recommended by other authors.

A summary of the critical point parameters for bismuth, available in the literature, is presented in Table 2.14.2.
Table 2.14.2. Summary of the critical point data of bismuth

<table>
<thead>
<tr>
<th>Reference</th>
<th>(T_c) [K]</th>
<th>(p_c) [MPa]</th>
<th>(\rho_c) [kg/m(^3)]</th>
<th>(Z_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Grosse, 1961]</td>
<td>4620</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cahill, 1968]</td>
<td>5000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fortov, 1975]</td>
<td>4200</td>
<td>126</td>
<td>2660</td>
<td>0.28</td>
</tr>
<tr>
<td>[Martynyuk, 1998]</td>
<td>3780</td>
<td>132</td>
<td>3010</td>
<td>0.29</td>
</tr>
<tr>
<td>[Azad, 2005]</td>
<td>2042-2106</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

There is still a very large uncertainty in the available data. For the time being, we recommend the mean rounded values reported by Fortov [Fortov, 1975] and by Martynyuk [Martynyuk, 1998] as the more complete and consistent data set:

\[ T_{c\text{Bi}} = 3990 \text{ K (3717°C)}, p_{c\text{Bi}} = 130 \text{ MPa}, \rho_{c\text{Bi}} = 2890 \text{ kg/m}^3 \] (2.47)

The recommended above values for the critical parameters of lead and bismuth are reasonable in comparison with the experimental data [Martynyuk, 1983] if we consider the experimental uncertainty estimated as \(\pm50\%\) for \(p_c\), \(\pm15\%\) for \(T_c\), and \(\pm20\%\) for \(\rho_c\).

2.14.1.3 LBE

Only two sets of the critical parameters of LBE are available in the published literature. One is proposed by K. Morita, et al. [Morita, 2004, 2005] and another by A-M. Azad [Azad, 2005]. Both were estimated theoretically on the basis of known properties for LBE. No publications are currently available with the results of measurement of the LBE critical parameters.

K. Morita, et al. [Morita, 2004, 2005] used the method proposed by Martynyuk [Martynyuk, 1998], which is based on the following generalised relationship:

\[ p = \frac{RT}{V - b} - \frac{a}{V^n} \] (2.48)

where \(a\), \(b\) and \(n\) are constants that must be determined. In [Martynyuk, 1998] these constants are expressed through the melting and boiling temperatures, the latent heats of melting and boiling, and the liquid molar volume in the melting and boiling points. In their calculations, Morita [Morita, 2004, 2005] took the liquid density from [Alchagirov, 2003] and calculated the heat of vaporisation from the Clapeyron equation using their estimated vapour pressure curve. The critical parameters of LBE obtained by them are \(T_{c\text{LBE}} = 4890 \text{ K (4617°C)}, \rho_{c\text{LBE}} = 2170 \text{ kg/m}^3\) and \(p_{c\text{LBE}} = 87.8 \text{ MPa}\).

M-A. Azad [Azad, 2005] estimated the LBE critical temperatures using a simple equation of state (EOS) for the liquid phase based on the concept of internal pressure of liquids and assuming that data on density, heat capacity and sound velocity are known:

\[ \frac{p + p_i}{T} = u_{\text{sound}} \alpha_p \rho \frac{C_p}{C_v} \] (2.49)

where \(p_i\) is the internal pressure, \(u_{\text{sound}}\) is the sound velocity, \(\alpha_p\) is the volumetric thermal expansion coefficient and \(C_p\) and \(C_v\) are the isobaric and isochoric heat capacities, respectively. The right side of Eq. (2.49) has been described with a linear empirical function of the form:
The gas phase was described with the perfect gas equation. In order to determine the constants $A$ and $B$, the LBE melt density was taken from the measurements of B.B. Alchagirov [Alchagirov, 2003]. The LBE heat capacity and the sound velocity were computed with Vegard’s law using the literature data on heat capacities [Kubaschewski, 1979], [Hultgren, 1974] and sound velocities [Mustafin, 1983], [Jarzynski, 1963] of lead and bismuth. The calculated values for the LBE critical temperature and pressure are $T_{c,LBE} = 2411$ K ($2138^\circ$C) and $p_{c,LBE} = 244$ MPa. It should be noted that the critical temperature of LBE obtained by Azad [Azad 2005] is more than by factor 2 lower and the critical pressure is 3 times higher than those calculated by Morita, et al. [Morita, 2004, 2005]. A summary of the critical parameters of LBE is given in Table 2.14.3.

### Table 2.14.3. Summary of the critical point data for LBE

<table>
<thead>
<tr>
<th>Reference</th>
<th>$T_c$ [K]</th>
<th>$p_c$ [MPa]</th>
<th>$\rho_c$ [kg/m$^3$]</th>
<th>$Z_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Morita, 2004]</td>
<td>4890</td>
<td>87.8</td>
<td>2170</td>
<td>—</td>
</tr>
<tr>
<td>[Azad, 2005]</td>
<td>2411</td>
<td>244</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

A very large uncertainty still exists in the estimation of the LBE critical parameters. More detailed analysis and comparison with other heavy metals is needed in order to provide recommendations. One of the reasons for a lower critical temperature obtained in the calculations of Azad may be the use of an incorrect temperature dependence of the sound velocity. In the absence of better data, the rounded values obtained by K. Morita, et al. [Morita, 2004] are recommended for very approximate estimations:

$$T_{c,LBE} = 4890$$ K ($4617^\circ$C), $p_{c,LBE} = 88$ MPa, $\rho_{c,LBE} = 2170$ kg/m$^3$

### 2.14.2 Equation of state

The vapour EOS for LBE was developed by K. Morita, et al. [Morita, 2004, 2005] for use in reactor safety analysis. They used the modified Redlich-Kwong (MRK) equation extended to a reacting system [Morita, 1998a], where the dimmer and monomer components consist of vapour. The functional form of the MRK equation extended to a reacting system is as follows:

$$p = \frac{RT}{M(1 + y_2)\left(v - a_1\right)} - \frac{a(T)}{v(v + a_3)}$$

with:

$$a(T) = a_2 \left(\frac{T}{T_c}\right)^{a_3}, \quad T \leq T_c$$

$$a(T) = a_2 + \frac{da}{dT}\bigg|_{T_c} (T - T_c), \quad T > T_c$$

where $p$ is the pressure, $T$ is the temperature, $v$ is the specific volume, $y_2$ is the dimer fraction, and $a_1$, $a_2$, $a_3$, and $a_4$ are the model parameters. From the definition, $y_2$ is related to the equilibrium constant $k_2$ given by:
where the total pressure \( p \) is the sum of the monomer pressure \( p_1 \) and the dimer pressure \( p_2 \):

\[
p = p_1 + p_2
\]

Although Eq. (2.52) was originally developed by Morita [Morita, 1998b] for sodium with dimerisation, it was applied to LBE assuming that LBE vapour consists of monatomic and diatomic components, representing the diatomic component of the LBE vapour as the diatomic bismuth. Therefore, Eq. (2.56) was given by:

\[
p_1 = p_{\text{Pb}} + p_{\text{Bi}}
\]

\[
p_2 = p_{\text{Bi}_2}
\]

where \( p_{\text{Pb}}, p_{\text{Bi}} \) and \( p_{\text{Bi}_2} \) are the partial pressure of monatomic lead, monatomic bismuth and diatomic bismuth, respectively.

The equilibrium constant of LBE, Eq. (2.55), was evaluated based on the vapour pressure data taken from the “best” values tabulated by R. Hultgren, et al. [Hultgren, 1974] for lead and bismuth as used for the estimation of the LBE vapour pressure. The results in the temperature range 700-2000 K (427-1727°C) were fitted to the following equation:

\[
k_2 = \exp \left( -24.611 + \frac{23511}{T} \right)
\]

where \( k_2 \) is in Pa\(^{-1}\) and \( T \) is in K.

The EOS parameters \( a_1, a_2 \) and \( a_3 \) in Eq. (2.52) were determined from the estimated values of critical constants [Morita, 2004, 2005], and the fact that the critical isotherm on a pressure-volume \( p-v \) diagram has an inflection point at the critical point. The parameter \( a_4 \) was fitted to the slope of the vapour pressure curve [Morita, 2004, 2005] at the critical temperature of 4617°C (4890 K). The resultant parameters are:

\[
\begin{align*}
a_1 &= 6.26824 \times 10^{-5}, \\
a_2 &= 1.59328 \times 10^2, \\
a_3 &= 8.11866 \times 10^{-4}, \\
a_4 &= 3.78359 \times 10^{-1}
\end{align*}
\]

A similar approach can be used for construction of the EOS for lead and bismuth.

2.15 Viscosity

Accurate and reliable data on viscosity of liquid metals are not abundant. Some discrepancies between experimental data can be attributed to the high reactivity of metallic liquids, to the difficulty of taking precise measurements at elevated temperatures, and to a lack of a rigorous formula for calculations. All liquid metals are believed to be Newtonian liquids. The temperature dependence of viscosity of liquid metals are usually described by an Arrhenius type formulae:
\[
\eta = \eta_0 \exp \left( \frac{E_\eta}{RT} \right)
\]  
(2.61)

where \( E_\eta \) is activation energy of motion for viscous flow.

In engineering hydrodynamics, the kinematic viscosity \( \nu \) is often used, which is a ratio of the dynamic viscosity \( \eta \) to the liquid density \( \rho \):

\[
\nu = \frac{\eta}{\rho}
\]
(2.62)

2.15.1 Lead


Figure 2.15.1 shows the values of molten lead viscosity taken from the cited literature.

**Figure 2.15.1. Lead dynamic viscosity as a function of temperature**

![Figure 2.15.1. Lead dynamic viscosity as a function of temperature](image-url)
Good agreement exists among the different sets of experimental data and the values calculated by means of the empirical equations. A reliable choice of an empirical equation to describe the temperature dependence of the dynamic viscosity of molten lead can be obtained by fitting the selected values into an Arrhenius type equation of the form:

$$\eta_{\text{mol}}[\text{Pa s}] = 4.55 \cdot 10^{-4} \cdot \exp \left( \frac{1069}{T} \right)$$

(2.63)

where temperature is in kelvins. This correlation is valid in the temperature range from \(T_{\text{melt}}\) to 1470 K (1197°C).

### 2.15.2 Bismuth

Most of analysed viscosity data for bismuth as a function of temperature are from about the same sources as for lead: [Lyon, 1954], [Kutateladze, 1959], [Bonilla, 1964], [Lucas, 1984b], [Iida, 1988] and Smithells Metal Reference Book [Smithells, 2004].

The values reported by Bonilla [Bonilla, 1964], are very high as compared with those given by the other sources, and those reported by Iida [Iida, 1988] are significantly lower. These data should be disregarded.


Figure 2.15.2 shows the values of viscosity taken from the cited literature for bismuth.

**Figure 2.15.2. Bismuth viscosity as a function of temperature**

![Bismuth viscosity graph](image-url)
A reasonable choice for an empirical correlation to calculate the bismuth viscosity as a function of temperature is that proposed by Smithells Metal Reference Book [Smithells, 2004]:

\[
\eta_{\text{Bi}}[\text{Pa s}] = 4.458 \cdot 10^{-4} \cdot \exp \left( \frac{775.8}{T} \right)
\]  

(2.64)

where temperature is in kelvins. This correlation is valid in the temperature range from \( T_{\text{melt}} \) to 1300 K (1027°C).

2.15.3 LBE

In the old Western sources, the recommendations for LBE viscosity are given for the temperature range of 300-700°C (673-973 K) by R.N Lyon [Lyon, 1954, 1960], C.L. Mantell [Mantell, 1958], and C.F. Bonilla [Bonilla, 1964]. At temperatures below 300°C (573 K) the data for the LBE kinematic viscosity are found in the publication of Kutateladze [Kutateladze, 1959]. New data were reported by J.P. Holman [Holman, 1968] and detailed measurements were performed later by B. Kaplun, et al. [Kaplun, 1979]. Recent data from [Kyrillov, 2000a] and [TECDOC -1289, 2002] are very close to those of [Kutateladze, 1959] up to about 900 K (627°C). At higher temperatures they deviate to higher values, probably, due to the presence of oxides or other impurities. The sources included in database are described in Table 2.15.1.

The data extracted from the selected sources are presented in Figure 2.15.3.

Table 2.15.1. Viscosity database for molten LBE

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.3.1</td>
<td>Dynamic viscosity</td>
<td>?</td>
<td>?</td>
<td>605-873</td>
<td>~10^5 (?)</td>
<td></td>
<td>[Lyon, 1954]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( \eta_{\text{LBE}}(T) = (5.37 - 8.92 \cdot 10^{-3} \cdot T + 4.71 \cdot 10^{-6} \cdot T^2) \cdot 10^{-3} \text{ Pa s} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.3.2</td>
<td>Kinematic viscosity</td>
<td>?</td>
<td>?</td>
<td>403-973</td>
<td>~10^5 (?)</td>
<td></td>
<td>[Kutateladze, 1959]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( \eta_{\text{LBE}}(T) = (2.077 - 8.983 \cdot 10^{-3} \cdot T + 1.629 \cdot 10^{-5} \cdot T^2 - 1.352 \cdot 10^{-8} \cdot T^3 + 4.25 \cdot 10^{-12} \cdot T^4) \cdot 10^{-2} \text{ Pa s} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.3.3</td>
<td>Dynamic viscosity</td>
<td>?</td>
<td>?</td>
<td>403-1073</td>
<td>~10^5 (?)</td>
<td></td>
<td>[Holman, 1968]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( \eta_{\text{LBE}}(T) = (4.56 - 7.03 \cdot 10^{-3} \cdot T + 3.61 \cdot 10^{-6} \cdot T^2) \cdot 10^{-3} \text{ Pa s} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.3.4</td>
<td>Dynamic viscosity</td>
<td>?</td>
<td>?</td>
<td>410-726</td>
<td>~10^5 (?)</td>
<td></td>
<td>[Kaplun, 1979]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function: ( \eta_{\text{LBE}}(T) = (1.702 - 6.612 \cdot 10^{-3} \cdot T + 1.064 \cdot 10^{-5} \cdot T^2 - 7.751 \cdot 10^{-9} \cdot T^3 + 2.118 \cdot 10^{-12} \cdot T^4) \cdot 10^{-2} \text{ Pa s} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The data on the LBE dynamic viscosity presented in Table 2.15.1 from [Kutateladze, 1959] have been calculated with Eq. (2.62) using the data on the kinematic viscosity and density presented in the same source.
Most of the discrepancies in the experimental data on LBE viscosity can be attributed to its high reactivity. This physical parameter is never additive for mixtures or alloys. Fitting the parameters of Eq. (2.61) to the viscosity database presented above yields the following correlation:

$$\eta_{LBE} = 4.94 \cdot 10^{-4} \cdot \exp \left( \frac{754.1}{T} \right)$$  \hspace{1cm} (2.65)

where temperature is in kelvins.

Eq. (2.65), along with the recommended correlations for the dynamic viscosity of molten lead and of molten bismuth, are also presented in Figure 2.15.3. It can be seen that viscosity of LBE is significantly lower than that of lead (especially at lower temperatures) and very close to the viscosity of bismuth. The maximum difference between the LBE viscosity given by (2.65) and the database set is about 6% are shown in Figure 2.15.4 in the temperature range of 400-1100 K (127-827°C).

The kinematic viscosity can be determined from Eq. (2.62) using the recommended correlations for the dynamic viscosity. Its dependence on temperature is illustrated by Figure 2.15.5. The kinematic viscosity of LBE is 1.2-1.5 times smaller than that of lead in the temperature range of 600-1100 K (327-827°C), but it is very close to the kinematic viscosity of bismuth.

### 2.16 Electrical resistivity

Metals in general are characterised by a very low electrical resistance, that increases with temperature and about doubles as a consequence of melting. The electrical resistivity of liquid metals with rare exceptions increases linearly with temperature (in the temperature region of interest) and therefore can be represented as follows:

$$r = r_0 + b_e \cdot T$$
Figure 2.15.4. Dispersion of the database set on the LBE dynamic viscosity from Eq. (2.65)

Figure 2.15.5. Kinematic viscosity of the melted lead, bismuth and LBE versus temperature
In general, the electrical resistivity of liquid metals increases, when impurities enter the melt. However, in the case of a liquid alloy system that is composed of polyvalent component, the resistivity sometimes shows a negative deviation from additivity of component resistivities.

2.16.1 Lead

The data on lead electrical resistivity as a function of temperature included in this handbook were taken from [Lyon, 1954, 1960], [Hofman, 1970], [Smithells, 1983, 2004], T. Iida and R.I.L. Guthrie [Iida, 1988], [Bretonnet, 1988], [Kyrillov, 2000a] and [TECDOC-1289, 2002].


A.J. Friedland [Friedland, 1966] reproduced data from [Lyon, 1960] and therefore was not included in the database.

Figure 2.16.1 shows the values of the electrical resistivity for molten lead taken from the literature cited above.

Figure 2.16.1. Electrical resistivity of molten lead versus temperature

The agreement between different sources is very good. Therefore, a reasonable choice of an empirical equation suitable for the calculation of the electrical resistivity of liquid lead as a function of temperature can be based on the coefficients given by Iida and Guthrie [Iida, 1988], i.e.:
which is valid in the temperature range of 601-1273 K (328-1000°C). The deviation of the selected data from this correlation is less than 1%.

2.16.2 Bismuth

The data for the electrical resistivity of molten bismuth included in this handbook were taken from [Lyon, 1954], [Iida, 1988] and [Bretonnet, 1988].


Figure 2.16.2 shows the values of electrical resistivity taken from literature for liquid bismuth, in the range of temperature of interest.

Figure 2.16.2. Electrical resistivity of liquid bismuth versus temperature

The amount of the available data on the electric resistivity of molten bismuth is limited, but the agreement between the three sources is good. Therefore, it is proposed to use an empirical correlation based on the coefficients given by J.L. Bretonnet [Bretonnet, 1988], i.e.:

\[ r_{\text{Bi}}[\Omega \text{ m}] = 0.971 \cdot 10^{-6} + 5.534 \cdot 10^{-10} \cdot T \]  

(2.67)

where temperature is in kelvins. The estimated deviation of other data from this correlation is about of 0.8% in the temperature range of 545-1420 K (272-1147°C).
2.16.3 LBE

Only two reliable data sources for the electric resistivity of molten LBE were found in the literature: [Lyon, 1954] (probably repeated by [Kutateladze, 1959]) and [TECDOC-1289, 2002]. A.J. Friedland [Friedland, 1966] reported only one value at 538°C (811 K). The data presented in Kyrillov and Bogoslovskaya [Kyrillov, 2000a] have been discarded because they give a very low electrical resistivity which is almost independent of temperature (later these data were corrected by P.L. Kyrillov in [TECDOC-1289, 2002]). The data from [Lyon, 1954] and [TECDOC-1289, 2002] were included in the database shown in Table 2.16.1.

Table 2.16.1. Electrical resistivity database for the melted LBE

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy %</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Interpolation function:</td>
<td>( r_{LBE} (T) = (89.343 + 0.05 \cdot T) \cdot 10^{-8} \Omega m )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.3.2</td>
<td>Electrical resistivity</td>
<td>?</td>
<td>?</td>
<td>403-1073</td>
<td>~ 10^5 (?)</td>
<td></td>
<td>[TECDOC-1289, 2002]</td>
</tr>
<tr>
<td></td>
<td>Interpolation function:</td>
<td>( r_{LBE} (T) = (83.325 + 0.0523 \cdot T) \cdot 10^{-8} \Omega m )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The experimental data are presented in Figure 2.16.3 together with those recommended for the electric resistivity of molten lead and of molten bismuth.

Figure 2.16.3. Electric resistivity of molten lead, bismuth and LBE versus temperature
In Figure 2.16.3 one can see that the LBE resistivity data recommended in [TECDOC-1289, 2002] fit very well the line calculated with the Vegard-Kopp law using the resistivities of lead and bismuth. The recommendations of Lyon [Lyon, 1954] yield higher values. Taking into account that the Vegard-Kopp law is not applicable in the general case to transport properties of binary systems, and that only two sources are available, all data points were included to in the development of the recommended linear interpolation correlation as follows:

\[
\rho_{\text{LBE}} \left[ \Omega \cdot \text{m} \right] = (86.334 + 0.0511 \cdot T) \cdot 10^{-8}
\]  

(2.68)

where temperature is in kelvins.

The deviation of the data recommended in [Lyon, 1954] and [TECDOC-1289, 2002] for the electric resistivity of molten LBE at normal conditions is illustrated in Figure 2.16.4. The maximum difference does not exceed 2.5% in the temperature range of 400-1100 K (127-823°C).

**Figure 2.16.4. Deviation of the experimental data on the electric resistivity of LBE from the recommended Eq. (2.68)**

2.17 Thermal conductivity and thermal diffusivity

Experimental determination of thermal conductivity of liquid metals is difficult because of the problems related to convection and to wetting. At present, few experimental data are available. Moreover, large discrepancies can exist between different sets of data. The high thermal conductivity of liquid metals is mainly due to free electrons. A simple theoretical relation exists for pure metals between electrical and thermal conductivities known as Wiedemann-Franz-Lorenz law [Kittel, 1956]:

\[
\lambda_e = L_0 \cdot T / r
\]

(2.69)

where \( \lambda_e \) is the electronic thermal conductivity, \( r \) is the electrical resistivity and \( L_0 = 2.45 \cdot 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^2 \) is the Lorenz Number.

82
This law has been confirmed for many liquid metals [Giordanengo, 1999]. The contribution of phonons to the thermal conductivity of metals of interest is small and can be neglected in the temperature range of 400-1200 K (127-927°C). Therefore, the approximate prediction of thermal conductivity of liquid metals and alloys is possible by combining the Wiedemann-Franz-Lorenz law and the existing, reliable values of the electrical resistivity.

2.17.1 Lead

The following data on lead thermal conductivity were analysed for the handbook: [Lyon, 1954], [Kutateladze, 1959], [Crean, 1964], Friedland [Friedland, 1966], Smithells [Smithells, 1983, 2004], [Jauch, 1986], [Iida, 1988], [Millis, 1996], [Kyrillov, 2000b], [TECDOC-1289, 2002] and Yamasue.


Friedland [Friedland, 1966] used values given in [Lyon, 1954] and in [Kutateladze, 1959]. U. Jauch and B. Shultz [Jauch, 1986] took their data from [Touloukian, 1970], that have been taken into account in [Millis, 1996]. These sources were not included in the database.

Figure 2.17.1 shows the values for lead thermal conductivity taken from the literature cited above. A very large dispersion of data is present from different sources. A decrease of the lead thermal conductivity with temperature reported by Lyon [Lyon, 1954] (also by L.E. Crean, W.E. Parkins [Crean, 1964], and M.J. Duggin [Duggin, 1972]) and an anomaly reported by S.S. Kutateladze, et al. [Kutateladze, 1959] can be attributed to oxidation effects.

![Figure 2.17.1. Thermal conductivity of molten lead versus temperature](image-url)
In an effort to find a physically reasonable compromise between the available data and taking into account the Wiedemann-Franz-Lorenz law, a linear correlation was chosen as recommendation for the thermal conductivity of molten lead:

$$\lambda_{\text{Pb}} \left[ \text{W m}^{-1} \text{ K}^{-1} \right] = 9.2 + 0.011 \cdot T$$  \hspace{0.5cm} (2.70)

where temperature is in kelvins. This correlation is applicable in the temperature range of $T_{\text{melt}}=1300 \text{ K}$ (1027°C).

### 2.17.2 Bismuth

The data for bismuth thermal conductivity reported in this handbook were taken from Lyon [Lyon, 1954], Kutatuladze [Kutatuladze, 1959], Crean and Parkins [Crean, 1964], Smithells Metal Reference Book [Smithells, 1983, 2004], Iida and Guthrie [Iida, 1988] and Millis, et al. [Millis, et al., 1996].

Smithells [Smithells, 1983] recommended the bismuth thermal conductivity values based on the results of [Samsonov, 1969], [Viswanath, 1972], [Bush, 1963] and [Stull, 1956]. Iida and Guthrie [Iida, 1988] used values taken from Powel [Powel, 1972]. Millis [Millis, 1996] initially reviewed the available data on bismuth thermal conductivity from the compilation of Touloukian [Touloukian, 1970] and then analysed more recent data. He used linear correlations expressing thermal conductivity as a function of temperature. Satisfactory agreement was found between values measured by Filippov [Filippov, 1973] and those derived using the Wiedemann-Franz-Lorenz law and the electric resistivity reported by [Iida, 1988].

Figure 2.17.2 shows the values of thermal conductivity taken from the literature for liquid bismuth, plotted in the range of temperatures of interest.

**Figure 2.17.2. Thermal conductivity of molten bismuth versus temperature**

![Thermal conductivity of molten bismuth versus temperature](image-url)
A discrepancy exists between the values taken from [Crean, 1964], that indicate a decrease of the Bi thermal conductivity with temperature up to 650 K (377°C) (not shown) and a constant value at higher temperatures, and the data given by the other sources. This source was not included in the database.

In this version of the handbook, the following empirical correlation recommended by K.C. Millis, et al. [Millis, et al., 1996] was chosen:

$$\lambda_{\text{Bi}} \left[ \text{W m}^{-1} \text{K}^{-1} \right] = 12 + 1 \cdot 10^{-2} \cdot (T - T_{\text{melt}}) = 6.55 + 1 \cdot 10^{-2} \cdot T$$  \hspace{1cm} (2.71)

where temperature is in kelvins, and which is applicable in the temperature range from $T_{\text{melt}}$ to about 1000 K (727°C).

### 2.17.3 LBE

Information on thermal conductivity for molten LBE mainly comes from the old handbooks [Lyon, 1954] and [Kutateladze, 1959]. Later handbooks or reviewers reference these data. Only in the handbook of Iida [Iida, 1988] did some values appear that differ from those cited above. In the Russian literature new data were summarised in the handbook of Kirillov [Kirillov, 2000b] without direct references to the sources. Later, the last recommendations were practically reproduced in [TECDOC-1289, 2002]. The data from these four sources for LBE thermal conductivity were included in the database described in Table 2.17.1.

**Table 2.17.1. Thermal conductivity database for the melted LBE**

<table>
<thead>
<tr>
<th>Reg. no.</th>
<th>Parameter</th>
<th>Measurement method</th>
<th>Estimated accuracy %</th>
<th>Temperature range, K</th>
<th>Pressure range, Pa</th>
<th>Values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.3.1</td>
<td>Thermal conductivity</td>
<td>Absolute</td>
<td>5% (?)</td>
<td>473-593</td>
<td>~ $10^5$</td>
<td></td>
<td>[Lyon, 1954]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Interpolation function:</td>
<td>$\lambda_{\text{LBE}}(T) = 3.48 + 0.0129 \cdot T$ W m$^{-1}$ K$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.3.2</td>
<td>Thermal conductivity</td>
<td>Comparative</td>
<td>?</td>
<td>403-973</td>
<td>~ $10^5$ (?)</td>
<td></td>
<td>[Kutateladze, 1959]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Interpolation function:</td>
<td>$\lambda_{\text{LBE}}(T) = 6.86 + 0.0102 \cdot T$ W m$^{-1}$ K$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.3.3</td>
<td>Thermal conductivity</td>
<td>?</td>
<td>?</td>
<td>~ $10^5$ (?)</td>
<td></td>
<td></td>
<td>[Iida, 1988]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Interpolation function:</td>
<td>$\lambda_{\text{LBE}}(T) = -1.25 + 3.04 \cdot 10^{-2} \cdot T - 1.343 \cdot 10^{-5} \cdot T^2$ W m$^{-1}$ K$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.3.4</td>
<td>Thermal conductivity</td>
<td>?</td>
<td>?</td>
<td>403-1073</td>
<td>~ $10^5$ (?)</td>
<td></td>
<td>[Kyrillov, 2000a]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Interpolation function:</td>
<td>$\lambda_{\text{LBE}}(T) = 7.03 + 0.000993 \cdot T$ W m$^{-1}$ K$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Comments: 44.5 wt.% Pb + 55.5 wt.% Bi. Unknown purity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The values of the LBE thermal conductivity extracted from the selected sources are presented in Figure 2.17.3 together with the recommended values for lead and bismuth.
A non-negligible difference exists between the old Western and Russian recommendations, the latter giving 15-20% higher values. The recommendation of Iida [Iida, 1988] provides intermediate values. The data from the handbook of Kyrillov [Kyrillov, 2000a] probably reproduce the old results of Kutateladze [Kutateladze, 1959].

Similar to viscosity and electric resistivity, the results on thermal conductivity are strongly affected by the purity of LBE. Thermal conductivity is not an additive parameter and therefore the Vegard-Kopp law cannot be used to estimate it. Contrarily, the Wiedemann-Franz law, which is valid for most metals, can be used.

Substituting in Eq. (2.69) the above recommended correlation for the LBE electrical resistivity, one can obtain the following correlation for the thermal conductivity of molten LBE:

\[
\lambda_{LBE} \approx \frac{2.45 \cdot T}{86.334 + 0.0511 \cdot T} \quad (2.72)
\]

where temperature is in kelvins.

Eq. (2.72) gives values close to the recommendations of Iida [Iida, 1988] at lower temperatures: 400-550 K (127-277°C), and close to the recommendations of [TECDOC-1289, 2002] at higher temperatures: 600-1100 K (327-827°C).

Fitting the data of Lyon [Lyon, 1954], Kutateladze [Kutateladze, 1959] and Iida [Iida, 1988] with a parabolic function yields the following recommended correlation:

\[
\lambda_{LBE} \approx 3.61 + 1.517 \cdot 10^{-2} \cdot T - 1.741 \cdot 10^{-6} \cdot T^2 \quad (2.73)
\]

where temperature is in kelvins.
The difference between the selected data and the recommended Eq. (2.73) is plotted in Figure 2.17.4.

The maximum deviation is 10-15\% at low temperatures. The Wiedemann-Frantz law can be used for an estimate of the LBE thermal conductivity if its electrical resistivity is known.

Thermal diffusivity is defined as follows:

\[ a_p = \frac{\lambda}{\rho \cdot c_p} \]  \hspace{1cm} (2.74)

So, it can be calculated using data for thermal conductivity, density and specific heat. Fitting the obtained data with a linear function yields the following correlation for LBE which can be recommended for practical use:

\[ a_{p,\text{LBE}} \left[ \text{m s}^{-2} \right] = \left(1.408 + 0.0112 \cdot T\right) \cdot 10^{-6} \]  \hspace{1cm} (2.75)

where temperature is in kelvins.

The calculated thermal diffusivities of lead, bismuth and LBE are plotted as a function of temperature in Figure 2.17.5.
2.18 Conclusions

The data on thermophysical properties of molten lead, bismuth and LBE are generally characterised by significant uncertainty (the exception is the melting point). In general, the reliability of data is satisfactory and good agreement among the different sources of experimental data is often observed. However, a large uncertainty still exists on heat capacity and thermal conductivity – different sources give even different temperature dependence of these parameters. A significant uncertainty also exists in the boiling temperature. The critical temperatures, the critical densities and the critical pressures of Pb, Bi and LBE are not well defined, and this hinders the development of equations of states for these coolants.

On the basis of the review of the data and recommendations available in the literature and of the recent compilations performed in ENEA and SCK•CEN for thermophysical properties of molten lead, bismuth and LBE, correlations are proposed that can serve as temporary recommendations for engineering estimations and design calculations.

The recommended correlations for main thermophysical properties of molten lead, bismuth and LBE are summarised in Tables 2.18.1 to 2.18.3.
<table>
<thead>
<tr>
<th>Property, parameter</th>
<th>SI unit</th>
<th>Correlation</th>
<th>Temperature range (K)</th>
<th>Estimated error ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting temperature</td>
<td>K</td>
<td>$T_{\text{melt}} = 600.6$</td>
<td>n/a</td>
<td>0.1</td>
</tr>
<tr>
<td>Latent heat of melting</td>
<td>kJ kg$^{-1}$</td>
<td>$Q_{\text{melt}} = 23.8$</td>
<td>n/a</td>
<td>0.7</td>
</tr>
<tr>
<td>Boiling temperature</td>
<td>K</td>
<td>$T_{\text{boil}} = 2016$</td>
<td>n/a</td>
<td>10</td>
</tr>
<tr>
<td>Latent heat of boiling</td>
<td>kJ kg$^{-1}$</td>
<td>$Q_{\text{boil}} = 858.2$</td>
<td>n/a</td>
<td>1.9</td>
</tr>
<tr>
<td>Saturated vapour pressure</td>
<td>Pa</td>
<td>$P_s = 6.189 \times 10^9 \cdot \exp(-22216/T)$</td>
<td>610-2016</td>
<td>15%</td>
</tr>
<tr>
<td>Surface tension</td>
<td>N m$^{-1}$</td>
<td>$\sigma = 0.519 - 1.13 \times 10^{-4} \cdot T$</td>
<td>601-1200</td>
<td>5%</td>
</tr>
<tr>
<td>Density</td>
<td>kg m$^{-3}$</td>
<td>$\rho = 11367 - 1.1944 \cdot T$</td>
<td>601-1900</td>
<td>0.7%</td>
</tr>
<tr>
<td>Sound velocity</td>
<td>m s$^{-1}$</td>
<td>$u_{\text{sound}} = 1951.75 - 0.3423 \cdot T + 7.635 \times 10^{-5} \cdot T^2$</td>
<td>601-2000</td>
<td>0.05% ?</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>Pa</td>
<td>$B_s = (42.15 - 1.652 \times 10^{-2} \cdot T + 3.273 \times 10^{-6} \cdot T^2) \times 10^9$</td>
<td>601-2000</td>
<td>–</td>
</tr>
<tr>
<td>Isobaric specific heat</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>$c_p = 175.1 - 4.961 \times 10^{-2} \cdot T + 1.985 \times 10^{-5} \cdot T^2$ \ - \ 2.099 \times 10^{-9} \cdot T^3 \ - \ 1.524 \times 10^{-6} \cdot T^2$</td>
<td>601-1300</td>
<td>7% ?</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>Pa s</td>
<td>$\eta = 4.55 \times 10^{-4} \cdot \exp(1069/T)$</td>
<td>601-1470</td>
<td>4%</td>
</tr>
<tr>
<td>Electric resistivity</td>
<td>$\Omega m$</td>
<td>$\rho = (66.6 + 0.0479 \cdot T) \times 10^8$</td>
<td>601-1300</td>
<td>1%</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>W m$^{-1}$ K$^{-1}$</td>
<td>$\lambda = 9.2 + 0.011 \cdot T$</td>
<td>601-1300</td>
<td>10% ?</td>
</tr>
<tr>
<td>Property, parameter</td>
<td>SI unit</td>
<td>Correlation</td>
<td>Temperature range (K)</td>
<td>Estimated error ±</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>-----------</td>
<td>--------------------------------------------------</td>
<td>-----------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>K</td>
<td>$T_{\text{melt}} = 544.4$</td>
<td>n/a</td>
<td>0.3</td>
</tr>
<tr>
<td>Latent heat of melting</td>
<td>kJ kg$^{-1}$</td>
<td>$Q_{\text{melt}} = 52.6$</td>
<td>n/a</td>
<td>1.7</td>
</tr>
<tr>
<td>Boiling temperature</td>
<td>K</td>
<td>$T_{\text{boil}} = 1806$</td>
<td>n/a</td>
<td>51</td>
</tr>
<tr>
<td>Latent heat of boiling</td>
<td>kJ kg$^{-1}$</td>
<td>$Q_{\text{boil}} = 857$</td>
<td>n/a</td>
<td>20</td>
</tr>
<tr>
<td>Saturated vapour pressure</td>
<td>Pa</td>
<td>$p_s = 2.4723 \times 10^{10} \cdot \exp(-22858/T)$</td>
<td>600-1806</td>
<td>70%</td>
</tr>
<tr>
<td>Surface tension</td>
<td>N m$^{-1}$</td>
<td>$\sigma = 0.4255 - 8.0 \times 10^{-5} \cdot T$</td>
<td>545-1300</td>
<td>5%</td>
</tr>
<tr>
<td>Density</td>
<td>kg m$^{-3}$</td>
<td>$\rho = 10726 - 1.2208 \cdot T$</td>
<td>545-1300</td>
<td>0.4%</td>
</tr>
<tr>
<td>Sound velocity</td>
<td>m s$^{-1}$</td>
<td>$u_{\text{sound}} = 2111.3 - 0.7971 \cdot T$</td>
<td>545-603</td>
<td>0.1%</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>Pa</td>
<td>$B_v = (44.67 - 0.0299 \cdot T) \times 10^9$</td>
<td>545-603</td>
<td>–</td>
</tr>
<tr>
<td>Isobaric specific heat</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>$c_p = 118.2 - 5.934 \times 10^{-1} \cdot T + 71.83 \times 10^{3} \cdot T^2$</td>
<td>545-1300</td>
<td>7%</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>Pa s</td>
<td>$\eta = 4.458 \times 10^{-4} \cdot \exp(775.8/T)$</td>
<td>545-1300</td>
<td>5%</td>
</tr>
<tr>
<td>Electric resistivity</td>
<td>$\Omega$ m</td>
<td>$r = (97.1 + 0.05534 \cdot T) \times 10^{-8}$</td>
<td>545-1420</td>
<td>0.8%</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>W m$^{-3}$ K$^{-1}$</td>
<td>$\lambda = 6.55 + 0.01 \cdot T$</td>
<td>545-1000</td>
<td>10%</td>
</tr>
</tbody>
</table>
Table 2.18.3. Summary of the recommended correlations for main thermophysical properties of molten LBE ($p \sim 0.1$ MPa)

<table>
<thead>
<tr>
<th>Property, parameter</th>
<th>SI unit</th>
<th>Correlation</th>
<th>Temperature range (K)</th>
<th>Estimated error ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting temperature</td>
<td>K</td>
<td>$T_{\text{melt}} = 397.7$</td>
<td>n/a</td>
<td>0.6</td>
</tr>
<tr>
<td>Latent heat of melting</td>
<td>kJ kg$^{-1}$</td>
<td>$Q_{\text{melt}} = 38.6$</td>
<td>n/a</td>
<td>0.2</td>
</tr>
<tr>
<td>Boiling temperature</td>
<td>K</td>
<td>$T_{\text{boil}} = 1943$</td>
<td>n/a</td>
<td>10</td>
</tr>
<tr>
<td>Latent heat of boiling</td>
<td>kJ kg$^{-1}$</td>
<td>$Q_{\text{boil}} = 854$</td>
<td>n/a</td>
<td>2.0</td>
</tr>
<tr>
<td>Saturated vapour pressure</td>
<td>Pa</td>
<td>$p_s = 11.1 \times 10^9 \cdot \exp(-22552/T)$</td>
<td>508-1943</td>
<td>50%</td>
</tr>
<tr>
<td>Surface tension</td>
<td>N m$^{-1}$</td>
<td>$\sigma = (437.1 - 0.066 \cdot T) \times 10^{-3}$</td>
<td>423-1400</td>
<td>5.0%</td>
</tr>
<tr>
<td>Density</td>
<td>kg m$^{-3}$</td>
<td>$\rho = 11096 - 1.3236 \cdot T$</td>
<td>403-1300</td>
<td>0.8%</td>
</tr>
<tr>
<td>Sound velocity</td>
<td>m s$^{-1}$</td>
<td>$u_{\text{sound}} = 1773 + 0.1049 \cdot T - 2.873 \times 10^{-4} \cdot T^2$</td>
<td>403-1300</td>
<td>–</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>Pa</td>
<td>$B_s = (35.18 - 1.541 \times 10^{-3} \cdot T - 9.191 \times 10^{-6} \cdot T^2) \cdot 10^9$</td>
<td>430-605</td>
<td>0.05%</td>
</tr>
<tr>
<td>Isobaric specific heat</td>
<td>J kg$^{-1}$</td>
<td>K$^{-1}$</td>
<td>$c_p = 159 - 2.72 \times 10^{-4} \cdot T + 7.12 \times 10^{-6} \cdot T^2$</td>
<td>430-605</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>Pa s</td>
<td>$\eta = 4.94 \times 10^{-4} \cdot \exp(754.1/T)$</td>
<td>400-1100</td>
<td>5%</td>
</tr>
<tr>
<td>Electric resistivity</td>
<td>$\Omega$</td>
<td>m</td>
<td>$r = (86.334 + 0.0511 \cdot T) \cdot 10^{-8}$</td>
<td>403-1100</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>W m$^{-1}$</td>
<td>K$^{-1}$</td>
<td>$\lambda = 3.61 + 1.517 \times 10^{-2} \cdot T - 1.741 \times 10^{-6} \cdot T^2$</td>
<td>403-1100</td>
</tr>
</tbody>
</table>
REFERENCES


Douglas, T.B., J.L. Dever (1953), Report NBS-2544, NBS, USA.


Eucker, A. (1936), Metallwirtsch, 15, 63.


Hiers, G.O. (1948), Metals Handbook, Cleveland, Ohio, USA.


Holman, J.P. (1968), Heat Transfer, MacGraw-Hill, USA.


Hultgren, R., et al. (1963), Selected Values of the Thermodynamic Properties, J. Wiley, USA.

Hultgren, R., et al. (1973), Selected Values of the Thermodynamic Properties of Binary Alloys, ASM, Metals Park, Ohio, USA.


Ruppersberg, H., W. Speicher (1976), Z. Naturforschung, 319, 47.


Steinberg, D.J. (1974), Met. Trans., 5, 1341.


TECDOC-1289 (2002), Comparative Assessment of Thermophysical and Thermohydraulic Characteristics of Lead, lead-bismuth and Sodium Coolants for Fast Reactors, IAEA, Vienna.


Chapter 3

THERMODYNAMIC RELATIONSHIPS AND HEAVY LIQUID METAL INTERACTION WITH OTHER COOLANTS*

3.1 Introduction

This chapter collects some thermodynamics data of Pb and Pb-Bi alloys and some solubility and diffusivity values of various elements in liquid Pb and LBE. Moreover, the interaction of liquid Pb and LBE with some coolant candidates such as water, sodium or oil is also considered.

3.2 Enthalpies, entropies (solid and liquid state) – free energy and entropy of mixing

The heats of formation of six solid Pb-Bi alloys have been measured at 400 K in a liquid lead solution calorimeter by P. Roy, et al. They found that these alloys obey Kopp’s law of additivity and the heats of formation are therefore temperature independent. The lead and bismuth used in these experiments were reported to be of 99.999% pure. With their results, they calculated integral free energies and entropies of formation for solid Pb-Bi alloys at 400 K as a function of the Pb content.

The main thermodynamic functions of interest are enthalpy $H$, free energy $F$, Gibbs potential $\Phi$ and entropy $S$. The thermodynamic functions of pure substances in the “standard condensed state” can be presented as follows:

\[
H(T) = H(0) + \int_0^T C_p(T) \, dT + \Delta H_m(T_m) + \int_{T_m}^T C_p(T) \, dT
\]  

\[
S(T) = \int_0^T \frac{C_p(T)}{T} \, dT + \frac{\Delta H_m(T_m)}{T_m} + \int_{T_m}^T \frac{C_p(T)}{T} \, dT
\]

(For the considered systems it was supposed that $S^0(0) = 0$ in agreement with the third law of thermodynamics.)

\[
\Phi(T) = H(T) - T \cdot S(T)
\]

Usually the values of the thermodynamics functions are tabulated using the temperature of 298.15 K and the pressure of 1.01325×10^5 Pa as the reference standard state (STP).

The most important results of enthalpy measurement (often based on the measurement of the heat capacity) of bismuth, lead and LBE issued before 1968 were compiled and analysed by R. Hultgren.

* Chapter lead: Anne Terlain (CEA, France). For additional contributors, please see the List of Contributors included at the end of this work.
et al. (1973, 1974). Based on the selected sources, they provided the tables with the recommended values of enthalpy, entropy and isobaric specific heat for condensed and gas phases in a large temperature range starting from the standard temperature of 298.15 K to the normal boiling temperature. As the maximum temperature in the considered experiments was limited to about 870 K for Bi, 1270 K for Pb, the recommended data at higher temperatures were obtained by extrapolation. There is no measurement of the LBE enthalpy. Therefore it is proposed to use the Kopp’s law (see also Section 2.13.3 of Chapter 2) for its estimation at temperatures higher than the lead melting point.

A detailed table with the recommended values of enthalpy, entropy and heat capacity of lead was also given by L. Gurvich, et al. These data were obtained by fitting of the theoretical formulae to the available experimental results and then using them for estimation of the considered properties in the whole temperature range (from 298.15 K to $T_{\text{melt}}$).

In the later compilation of B. Cheynet (1996) the standard values of entropy of Pb and Bi ($S_{\text{Pb}}$ (298) = 64.785 J mol$^{-1}$ K$^{-1}$) were given together with the enthalpy tables for the range of 400-2000 K. For the liquid lead these recommendations differ for less than 0.2% from those of R. Hultgren up to 1900 K. Closer to the boiling point the difference increases to about 0.4%. For the bismuth, the results in the two works are practically identical (difference less than 0.08%).

The temperature dependence of the molten Pb and Bi enthalpies given in the references cited above are described, with deviation less than 0.5%, by the following parabolic correlations:

$$\Delta H_{\text{Pb}}^{(298)}(T) = -5.133 \cdot 10^{-4} \cdot T^2 + 30.3623 \cdot T - 4671.91$$

$$\Delta H_{\text{Bi}}^{(298)}(T) = -5.425 \cdot 10^{-4} \cdot T^2 + 28.8471 \cdot T - 2592.02$$

The enthalpy of LBE obtained using Eqs. (3.4), (3.5) and Kopp’s law (for LBE composition of 44.29 at.% Pb and 55.71 at.% Bi) can be presented as follows.

$$\Delta H_{\text{LBE}}^{(298)}(T) = -5.296 \cdot 10^{-4} \cdot T^2 + 29.5182 \cdot T - 3513.20$$

So as to be consistent with Chapter 2 of this handbook, the enthalpy was also calculated with Eq. (3.1) above and the recommended correlations for heat capacities of the molten Pb, Bi and LBE presented in Chapter 2. This transformation yields the following relationships:

$$H(T) - H(T_m) = 33.756 \cdot (T - T_m) - 3.131 \cdot 10^{-3} \cdot (T - T_m)^2 + 5.7614 \cdot 10^{-7} \cdot (T - T_m)^3$$

$$H_{\text{Bi}}(T) - H_{\text{Bi}}(T_m) = 24.7014 \cdot (T - T_m) + 6.200 \cdot 10^{-4} \cdot (T - T_m)^2 - 1.5011 \cdot 10^6 \cdot (T^{-1} - T_m^{-1})^4$$

$$H_{\text{LBE}}(T) - H_{\text{LBE}}(T_m) = 33.1025 \cdot (T - T_m) - 5.6628 \cdot 10^{-3} \cdot (T - T_m)^2 + 1.4823 \cdot 10^{-6} \cdot (T - T_m)^3$$

All the literature data together with the recommended curves based on Eqs. (3.7) and (3.8) are presented in Figures 3.2.1 and 3.2.2. Figure 3.2.3 presents the results of calculation of the LBE enthalpy together with those for Pb and Bi. The maximum deviation of the presented literature data from the proposed recommended curves does not exceed 1.6% for Bi and 5% for Pb.
Figure 3.2.1. Variations of the lead enthalpy with temperature

![Pb](image1)

Figure 3.2.2. Variations of the bismuth enthalpy with temperature

![Bi](image2)

Figure 3.2.3. Calculated values of the LBE enthalpy

![LBE](image3)
3.3 Purity requirements

The chemical composition of lead or LBE is of importance for the operating conditions of a nuclear system:

- First, the formation of radioactive elements due to irradiation induces a contamination of the circuits and components. It may also have an influence on physical parameters of the reactor.
- Second, a high content of some impurity elements in the coolant may have an effect on the coolant chemistry control and affecting the corrosion resistance of structural steels.
- Third, if some impurities react with other elements produced under irradiation, it can induce solid precipitation at the surface of the primary circuit components and may strongly affect thermal and hydraulic characteristics of the reactor. Moreover, mass transfer from a thermal gradient for example can induce precipitation of solids in the coldest parts of the circuit which may result in flow blockages or instabilities.

The main sources of impurities in the heavy metal coolant in nuclear systems are:

- metallic impurities due to the limits of the refining process and their ingress during casting;
- corrosion and erosion products resulting from the interaction of structural materials with the heavy liquid metal coolant;
- coolant interaction with gas in the circuit;
- spallation or fission products due to proton or neutron beam/material interactions;
- release of fission products to the coolant in case of clad rupture. Some important fission products are radio isotopes of iodine ($^{131}\text{I}$, $^{133}\text{I}$, $^{135}\text{I}$) and caesium ($^{134}\text{Cs}$, $^{136}\text{Cs}$, $^{137}\text{Cs}$);
- processes related to purposeful adding of impurities (oxygen for example) to the coolant.

In this chapter, we only look at the impurities in the lead or LBE before use. The impurities generated during operation are considered in Chapter 4 together with the methods for control and removal of them.

At the moment, no nuclear specifications exist for lead or LBE. However, different commercial materials seem to have an appropriate purity for nuclear applications. Commercial grades of lead content up to 99.98 wt.% of the basic metal are available. Typical lead and LBE impurity contents are given as examples in Table 3.3.1. [Ivanov, 2003] recommends C00 or C0 purity for lead and the chemical composition of LBE used for MEGAPIE experiment is given in Table 3.3.2 [Safety, 2002].

Silver is the only noticeable impurity which may be relevant for activation. It is activated under the neutron flux through the following reaction:

$$^{109}\text{Ag} (\text{n,}\gamma) ^{110}\text{mAg}, 250 \text{ d}$$

In addition to metallic impurities, there are some amounts of oxygen, nitrogen and hydrogen in the initial lead or LBE resulting from the conditions of cooling down of commercial material, overall dimensions of ingots and conditions of its further storage. Of concern is not only oxygen distributed in the volume of ingots but also oxygen in the near-surface layer of ingots as lead oxide (PbO). As a result of long storage of unprotected ingots in humid atmosphere, adsorbed moisture is transformed on their surface to the lead hydroxide in the reaction:

$$\text{PbO} + \text{H}_2\text{O} = \text{Pb(OH)}_2$$
Table 3.3.1. Chemical composition of commercial lead, wt.%

<table>
<thead>
<tr>
<th>Elements</th>
<th>Lead brand</th>
<th>Lead brand</th>
<th>Elements</th>
<th>Lead brand</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C00</td>
<td>C0</td>
<td>C1</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.00001</td>
<td>0.0004</td>
<td>0.001</td>
<td>Tl</td>
</tr>
<tr>
<td>Cu</td>
<td>0.00001</td>
<td>0.0005</td>
<td>0.001</td>
<td>Ca</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0001</td>
<td>0.001</td>
<td>0.001</td>
<td>Na</td>
</tr>
<tr>
<td>Bi</td>
<td>0.0005</td>
<td>0.004</td>
<td>0.006</td>
<td>Cd</td>
</tr>
<tr>
<td>As</td>
<td>0.0001</td>
<td>0.0005</td>
<td>0.001</td>
<td>Al</td>
</tr>
<tr>
<td>Sn</td>
<td>0.0001</td>
<td>0.0005</td>
<td>0.001</td>
<td>Hg</td>
</tr>
<tr>
<td>Sb</td>
<td>0.0001</td>
<td>0.0005</td>
<td>0.001</td>
<td>In</td>
</tr>
<tr>
<td>Mg</td>
<td>0.0001</td>
<td>–</td>
<td>–</td>
<td>Mg+Ca+Na</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0001</td>
<td>0.001</td>
<td>0.001</td>
<td>Pb</td>
</tr>
</tbody>
</table>

Table 3.3.2. Metallic impurities in the LBE for MEGAPIE experiment [Safety, 2002]

<table>
<thead>
<tr>
<th>Element</th>
<th>Content (μg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>25.6</td>
</tr>
<tr>
<td>Cd</td>
<td>2.2</td>
</tr>
<tr>
<td>Cr</td>
<td>0.19</td>
</tr>
<tr>
<td>Cu</td>
<td>26.5</td>
</tr>
<tr>
<td>Fe</td>
<td>1.4</td>
</tr>
<tr>
<td>In</td>
<td>14.4</td>
</tr>
<tr>
<td>Ni</td>
<td>2</td>
</tr>
<tr>
<td>Sn</td>
<td>5.9</td>
</tr>
</tbody>
</table>

3.4 Solubility data of metallic and non-metallic impurities in LBE and Pb

3.4.1 Solubility data of some metallic elements in pure Pb and liquid eutectic Pb-Bi

The procedures used for the determination of the solubility in the liquid metals cause some problems because subsequent chemical reaction or exchange of impurities (oxygen, nitrogen, carbon,...) between the liquid metal and the solid metal or compound may occur.

Generally, when the experimental technique is described, the solubility of a metallic element X in the considered liquid metals is obtained by putting the metal X (as a specimen or the crucible containing the melt) in contact with the liquid for several hours. Then a filtered few grams of this latter are sampled at the temperature of the test. The samples are then analysed. They are dissolved in a nitric acid solution and the X element content is measured by atomic absorption or by colorimetric techniques using some ortho-phenantroline for iron. When a constant X content is obtained, it is considered that the solubility value is reached and is taken equal to the constant value.

For a metallic element with a large solubility, a specimen is immersed in a liquid bath and the weight loss of the metallic specimen is regularly measured. When it is constant, then it is considered that the solubility of X element is reached. It is equal to the weight loss of the metallic specimen divided by the liquid bath volume.

A large amount of solubility data has been reported in [Tecdoc, 2002] (which is a compilation of data available in [Kozlov, 1983] and [Arnoldov, 1998]). The values of metallic solubility in LBE
mentioned by [Li, 2002] coming from [Gromov, 1997] [Orlov, 1997], [Adamov, 1998] are in agreement with those data. Table 3.4.1 gives the values of A, B of the equation used to characterise the solubility values as a function of temperature and the temperature range when it is specified.

\[ \log S \text{ (wt.\%)} = A - \frac{B}{T(K)} \]

Table 3.4.1. Solubility of some elements in liquid Pb, and Pb-Bi

<table>
<thead>
<tr>
<th>Element</th>
<th>Ref.</th>
<th>Pb T (°C)</th>
<th>A</th>
<th>B</th>
<th>LBE T (°C)</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>[Tecdoc, 2002]</td>
<td>330-1300</td>
<td>2.78</td>
<td>1000</td>
<td>450-550</td>
<td>1.7</td>
<td>1000</td>
</tr>
<tr>
<td>Ni</td>
<td>[Alden, 1958]</td>
<td>340-800</td>
<td>1.3</td>
<td>1383</td>
<td>400-900</td>
<td>1.53</td>
<td>843</td>
</tr>
<tr>
<td>Mn</td>
<td>[Pelzel, 1956]</td>
<td>474-1000</td>
<td>3.0445</td>
<td>3272</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>[Elliot, 1965]</td>
<td>350-800</td>
<td>6.32</td>
<td>2690</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>[Tecdoc, 2002]</td>
<td>350-1650</td>
<td>2.60</td>
<td>4400</td>
<td>400-550</td>
<td>1.3</td>
<td>2834</td>
</tr>
<tr>
<td>Cu</td>
<td>[Tecdoc, 2002]</td>
<td>327-1000</td>
<td>2.72</td>
<td>2360</td>
<td>400-550</td>
<td>2.41</td>
<td>1920</td>
</tr>
<tr>
<td>Fe</td>
<td>[Alden, 1958]</td>
<td>340-750</td>
<td>1.17</td>
<td>2900</td>
<td>550-800</td>
<td>2.01</td>
<td>4380</td>
</tr>
<tr>
<td>Cr</td>
<td>[Venkatraman, 1988]</td>
<td>3.70</td>
<td>6270</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>[Tecdoc, 2002]</td>
<td>908-1210</td>
<td>3.74</td>
<td>6750</td>
<td>400-500</td>
<td>-0.02</td>
<td>2280</td>
</tr>
<tr>
<td>Cr</td>
<td>[Venkatraman, 1988]</td>
<td>3.70</td>
<td>6270</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>[May, 1982]</td>
<td>600-700°C</td>
<td>&lt;10^-6 wt.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>[Tecdoc, 2002]</td>
<td>800-1200</td>
<td>1.6</td>
<td>6000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>Brewer (1980)</td>
<td>1.92</td>
<td>10553.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>[Tecdoc, 2002]</td>
<td>1050-1250</td>
<td>3.886</td>
<td>7180</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>[Tecdoc, 2002]</td>
<td>500</td>
<td>~1.2 10^-3 wt.%</td>
<td>227-725</td>
<td>0.15</td>
<td>3172</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>[Tecdoc, 2002]</td>
<td>1000</td>
<td>&lt; 10^-3 wt.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>[Tecdoc, 2002]</td>
<td>500</td>
<td>~5.6 10^-3 wt.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>[Tecdoc, 2002]</td>
<td>400-800</td>
<td>3.921</td>
<td>5121</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
N₂ is not soluble in lead or LBE.

In Figures 3.4.1 and 3.4.2 the different solubility data for iron in, Pb, Bi and LBE are compared. The iron solubility is higher in liquid Bi than in liquid Pb. It is intermediate in LBE.

**Figure 3.4.1. Solubility data of iron in liquid Pb, Bi and LBE**

A comparison of the solubility of some metallic elements of interest from a corrosion point of view shows that, as has been reported by [Borgstedt, 1992], these data follow the general trends in the solubility of transition metals reported by [Guminski, 1990]: Ni and Mn dissolve to a large extent in low melting point metals while molybdenum has a very low solubility.

**Figure 3.4.2. Solubility data of Fe, Cr, Ni in liquid Pb and LBE from [Tecdoc, 2002]**
3.4.2 Solubility data of oxygen in pure Pb and LBE

Different determinations of the oxygen solubility limit in Pb and Pb-Bi have been performed. At the lowest temperatures (~500°C), sampling methods are generally used. At higher temperature, experimental techniques rest on rare earth stabilised zirconia probes. These probes allow not only the measurement but also the control of dissolved oxygen in Pb-Bi.

Different techniques have been used to determine the solubility limit of oxygen in Pb-Bi. Among these are the following:

1) After oxygen has been inserted in the liquid Pb bath, the bath is sampled. The Pb sample is melted again in a graphite crucible. The CO2 production is then measured and converted to an oxygen concentration in the bath [Steen, 1982].

2) The oxygen content is obtained from calorimetric measurements [Rodigina, 1961].

3) Solid PbO is dissolved in the liquid and the oxygen content dissolved in the liquid is continuously measured by means of a rare earth stabilised zirconia probe [Taskinen, 1979].

4) Oxygen is introduced into the liquid by electrochemical techniques using a rare earth stabilised zirconia probe. The dissolved oxygen content is followed in parallel with a rare earth stabilised zirconia probe [Ghetta, 2002].

5) The oxygen solubility limit in LBE is deduced from the oxygen solubility limits in pure liquids Pb and Bi by thermodynamical calculations using free enthalpies of PbO and Bi2O3 oxides [Müller, 2003].

In a bibliographic review on the compatibility of structural steels with liquid lead, [Flament, 1988] reported on a study from [Steen, 1982] which compared the data obtained at temperatures lower than 550°C from various authors. These data are shown in Figure 3.4.3. [Steen, 1982] observed large discrepancies between them and concluded that the discrepancies probably are the consequence of the presence of stray oxide particles in the liquid lead and that in the 400-500°C temperature range, the oxygen solubility is low. From his work, he suggested a value of about 1 ppm.

Figure 3.4.3. Data of oxygen solubility in lead reported in [Steen, 1982]

1 – Reinert, 2 – Worner, 3 – Baker, 4 – Hansen, 5 – Bartfeld, 6 – Zausznica, 7 – Carlsson
Very recently, [Ganesan, 2006] reviewed some literature data on oxygen solubility in liquid Pb and LBE and presented new results. Based on the uncertainties on the data obtained from sampling methods [Risold, 1998], [Ganesan, 2006] considers only the data obtained mostly at high temperature by electrochemical methods.

Selected oxygen solubility data are reported in Table 3.4.2. The $A$ and $B$ parameters refer to the following equation:

$$\log (S \text{ wt.\%}) = A - \frac{B}{T}$$

<table>
<thead>
<tr>
<th>Pb</th>
<th>Tem $°\text{C}$</th>
<th>$A$</th>
<th>$B$</th>
<th>LBE</th>
<th>Tem $°\text{C}$</th>
<th>$A$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rodigina, 1961]</td>
<td>300-400</td>
<td>3.1</td>
<td>4900</td>
<td>[Gromov]</td>
<td>400-700</td>
<td>1.2</td>
<td>3400</td>
</tr>
<tr>
<td>[Heinz, 2002]</td>
<td>1.64</td>
<td>3603</td>
<td></td>
<td>[Martinov]</td>
<td>400-700</td>
<td>1.2</td>
<td>3400</td>
</tr>
<tr>
<td>[Isecke, 1977]</td>
<td>900-1100</td>
<td>3.38</td>
<td>5182</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Conochie, 1981]</td>
<td>800-845</td>
<td>3.38</td>
<td>5170</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Szwarc, 1972]</td>
<td>455-606</td>
<td>0.96</td>
<td>3007</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Gromov, 1999]</td>
<td>400-700</td>
<td>3.2</td>
<td>5000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.4.4 represents the high temperature experimental data on oxygen solubility in liquid lead obtained by electrochemical techniques. From this figure, it appears that the data of [Szwarc, 1972] deviate from the others. [Ganesan, 2006] explains that the use of chromel wire as electrical lead would have contributed to this deviation due to the interaction of dissolved Cr and Ni with oxygen in molten Pb. The other data are in agreement, except those of [Conochie, 1981] at low temperatures.

**Figure 3.4.4. Data of oxygen solubility in molten lead from Table 3.4.2**
Figure 3.4.5 compares the values of oxygen solubility in molten LBE reported in Table 3.4.2. Except the estimation of [Müller, 2003] from the corresponding binary data, there is a good agreement between the different data.

**Figure 3.4.5. Data of oxygen solubility in molten LBE**

![Graph showing data of oxygen solubility in molten LBE.](image)

The more generally used values for oxygen solubility are:

In lead: \( \log S \, (\text{wt.\%}) = 3.2 - \frac{5000}{T(K)} \)

In LBE: \( \log S \, (\text{wt.\%}) = 1.2 - \frac{3400}{T(K)} \)

### 3.5 Diffusivity

#### 3.5.1 Diffusivity data of some metallic elements

The diffusion coefficient of a solute in a melt is a fundamental quantity required to characterise mass-transport rates. However, there are numerous difficulties in accurately measuring diffusion coefficients in liquid metals, the main being the problem of mass transport by bulk motion of the fluid due to natural convection. This is driven by buoyancy forces produced by any temperature or concentration gradients which lead to decrease of liquid density with depth. Several different techniques exist to determine the diffusion coefficient in molten metals and generally their accuracy is of the order several %. A survey of these techniques is available in [Kubicek, 1983], [Shimoji, 1986].

*Experimental techniques*

Capillary techniques

Many diffusion coefficients in molten metals have been determined by means of capillary techniques. These techniques include:
1) **Capillary reservoir methods (with finite or semi-infinite capillary tubes).** In this technique a long capillary tube containing the pure molten metal is immersed in a large reservoir of the same molten metal containing a known concentration of the metal whose diffusion rate is desired to be measured. Concentration of the diffusing species is successfully determined by using radionuclides or X-ray spectral analysis.

Some specific arrangements have been developed to improve these methods. For example, it has been developed a shearing cell consisting in six discs that can rotate around an axial pin. The capillaries in three of the discs are filled with pure melt and a fourth is filled with melt containing a radioactive diffusing species. The outmost disc serves to close off the capillaries. As soon as the capillaries are aligned, diffusion starts. After a certain period, the discs are revolved to shear the column into four segments. Sometimes, the capillary reservoir method has been combined with use of high temperature galvanic cell in particular to determine the oxygen diffusion coefficients in various liquid metals. The main advantage of this method is that the diffusion coefficient is measured in situ, not by subsequent analysis.

2) **Stationary diffusion source methods.** With this method the species whose diffusion is to be investigated is allowed to come into contact with the liquid through a gaseous phase. This method avoids some of the shortcoming of the capillary reservoir technique and is efficient with radionuclides.

3) **Reactive diffusion methods.** With this method the solid phase is allowed to come into contact with the melt.

The above methods suffer from several shortcomings including convection (during immersion of the tube or due to difference of density, mechanical effects, thermal gradient), inaccurate initial or boundary conditions, surface diffusion, inaccuracy in determining the concentration profiles of the diffusing species or phenomena arising during solidification.

**Controlled forced convection techniques**

The errors due to convection can be suppressed by imposing controlled force convection. When the dissolution of a solid in a liquid is diffusion controlled in the liquid boundary layer, the method of rotating disc dissolution can be used. This method uses a rotating disc which dissolves in a static melt. The rate of rotation is chosen so that laminar flow is achieved. The weight loss of the disc combined with the time of dissolution and angular velocity allow determination of the diffusion coefficient. The control of convection can also be insured by applying electromagnetic stirring.

**Electrochemical methods**

Electrochemical techniques are especially suitable for the determination of diffusion coefficients in the melt because convection is suppressed or eliminated. The experiments last only few seconds in contrast to the capillary methods and the wall effects are not encountered. Of these methods, the most important in the study of diffusion in melts are chronopotentiometry and rotating disc electrode (RDE). Linear voltammetry and polarography have limited application.

In the chronopotentiometry method, a pulse of current density is used to disturb the system from its equilibrium and the potential variation with time of the investigated electrode is measured. In the rotating disc method, an increasing voltage is applied to the RDE and the current is measured. In the linear voltammetry method, an increasing potential is applied to the working electrode. The current intensity variations with time and its maximum are measured.
**Available data**

Only a few data for diffusion coefficients of metallic elements in liquid lead and lead bismuth are available in the literature. Special attention is paid to the iron coefficient because iron diffusion in liquid lead alloys is the limiting step of the corrosion of iron and iron chromium alloys such as T91 (Fe-9Cr).

The iron diffusion coefficient in Pb-Bi, is known at only three temperatures:

- 400° C: \(3.5 \times 10^{-7}\) cm\(^2\)/s [Balbaud 2004];
- 470° C: \(7.6 \times 10^{-6}\) cm\(^2\)/s [Balbaud, 2004];
- 750° C: \(2.27 \times 10^{-5}\) cm\(^2\)/s [Benerjee, 1974].

These data have been obtained by means of experiments with a rotating disk specimen [Benerjee, 1974] or a T91 steel (Fe-9Cr) cylinder [Balbaud, 2004]. The specimen dissolution rate is limited by iron diffusion in the boundary layer and is determined by a weight loss measurement. It depends on the temperature, time, rotating speed, liquid viscosity, the solubility and diffusivity of the solute.

The iron diffusion coefficient in lead has been determined by analysing the grooving of grain boundaries by the liquid metal [Robertson, 1968]. With this method the liquid metal in contact with the solid dissolves the grain boundaries to form grooves. The groove width is linked to the diffusion coefficient of solid elements in the liquid.

Figure 3.5.1 shows that the diffusion coefficients for iron in liquid Pb and LBE are not very different. The data determined at low temperature are not far from the extrapolated values for iron from high temperatures (700°C-1000°C) [Robertson, 1968].

The iron diffusion coefficient in LBE is approximated to that in lead and they correspond to the extrapolated values of [Robertson, 1968]:

\[
\log(D \text{ cm}^2/\text{s}) = -2.31 - \frac{2295}{T} \quad (700°C < T < 1000°C)
\]

**Figure 3.5.1. Iron diffusion coefficient in pure Pb and eutectic Pb-Bi**
Selected diffusion coefficient data for different metallic elements in lead are also reported in the literature and given in Table 3.5.1.

### Table 3.5.1. Diffusion coefficients of some metallic elements in lead liquid

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature range (°C)</th>
<th>Diffusion coefficient (cm² s⁻¹); ( R ) (J mol⁻¹ K⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>750-1000</td>
<td>( 4.6 \times 10^{-4} \exp(-22154/RT) )</td>
<td>[Robertson, 1968]</td>
</tr>
<tr>
<td>Se</td>
<td>550-900</td>
<td>( 3.4 \times 10^{-4} \exp(-12958/RT) )</td>
<td>[Lozovoy, 1981]</td>
</tr>
<tr>
<td>In</td>
<td>450-900</td>
<td>( 3.1 \times 10^{-4} \exp(-13794/RT) )</td>
<td>[Lozovoy, 1981]</td>
</tr>
<tr>
<td>Tl</td>
<td>450-900</td>
<td>( 3.1 \times 10^{-4} \exp(-15884/RT) )</td>
<td>[Lozovoy, 1981]</td>
</tr>
</tbody>
</table>

#### 3.5.2 Oxygen diffusion coefficient

Different techniques have been used to determine the oxygen diffusion coefficient.

1) Electrochemical measurement with a rare earth stabilised zirconia electrode [Szarc, 1972], [Bandyopadhyay, 1971], [Honma, 1971]: the principle is to perform amperometries at the oxygen reduction potential. The variations of the current intensity are related to the diffusion coefficient of oxygen in the lead.

2) Electrochemical measurements with a rare earth stabilised zirconia electrode on each side of a horizontal column of liquid lead. One probe is used to introduce oxygen into the liquid. The other, on the opposite side of the lead column is used to measure oxygen concentration as a function of time via its potential. This data is then to determine the oxygen coefficient diffusion coefficient.

3) Measurement of the weight loss of a PbO rotating disc [Gromov, 1996]. The dissolution kinetics of PbO in liquid lead or LBE depends on the oxygen solubility, the rotation speed of the disc, the viscosity of the liquid and the diffusion coefficient of oxygen at the temperature.

Selected oxygen diffusion coefficient data are given in Table 3.5.2 and Figure 3.5.2.

### Table 3.5.2. Data on oxygen diffusion coefficient in liquid lead and LBE

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Temperature range (°C)</th>
<th>Diffusion coefficient of oxygen (cm² s⁻¹); ( R ) (J mol⁻¹ K⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>700-900</td>
<td>( 6.32 \times 10^{-2} \exp(14979/RT) )</td>
<td>[Honma, 1971]</td>
</tr>
<tr>
<td>Pb</td>
<td>800-1100</td>
<td>((9.65 \pm 0.71)\times 10^{-5} \exp(-20083 \pm 6067/RT) )</td>
<td>[Honma, 1971]</td>
</tr>
<tr>
<td>Pb</td>
<td>750</td>
<td>(1.29 \times 10^{-3} )</td>
<td>[Bandyopadhyay, 1971]</td>
</tr>
<tr>
<td>Pb</td>
<td>740-1080</td>
<td>((1.44 \pm 0.45)\times 10^{-3} \exp(-25942 \pm 2803/RT) )</td>
<td>[Swzarc, 1972]</td>
</tr>
<tr>
<td>Pb</td>
<td>900-1100</td>
<td>((1.48 \pm 0.6) \times 10^{-3} \exp(-19497 \pm 10711/RT) )</td>
<td>[Otsuka, 1975]</td>
</tr>
<tr>
<td>Pb</td>
<td>900-1100</td>
<td>(1.90 \times 10^{-3} \exp(-20920/RT) )</td>
<td>[Charle, 1976]</td>
</tr>
<tr>
<td>Pb</td>
<td>400-1000</td>
<td>(6.6 \times 10^{-5} \exp(-16158/RT) )</td>
<td>[Gromov, 1996]</td>
</tr>
<tr>
<td>Pb-Bi</td>
<td>200-1000</td>
<td>(2.39 \times 10^{-5} \exp(-43073/RT) )</td>
<td>[Gromov, 1996]</td>
</tr>
</tbody>
</table>
The following observations are made:

1) The differences between the data in lead may result from the differences between materials used for the rare earth stabilised zirconia probe.
2) The results obtained with the rare earth stabilised zirconia probe are not very different from those obtained with a rotation disc.
3) There is a significant scatter of the different values except in the 600-700°C temperature range.
4) The oxygen diffusion coefficients in lead and LBE differ by two orders of magnitude.

**Figure 3.5.2. Oxygen diffusion coefficient in liquid lead and lead-bismuth**

![Oxygen diffusion coefficient graph](image)

**3.6 Chemical interactions and ternary phase diagrams**

During operation, lot of spallation products will be generated in the LBE target. In particular mercury is expected to be the most generated species. Therefore, the ternary Pb-Bi-Hg system has been investigated [Maître, 2002]. Phase limits and invariant equilibria were determined by differential Scanning Calorimetry (DSC). The phase diagram computation was performed using Calphad method [Kaufman, 1970] with Thermocal software.

Two isothermal sections at 310 K and 355 K of the ternary phase diagram are given in Figures 3.6.1 and 3.6.2.

The 310 K section emphasises a peritectic equilibrium:

\[ C = \text{Liq } + \text{Fcc (Pb)} + \text{Rhombo}_A7(Bi) \]

where \( C \) is \( \text{Bi}_{0.35} \text{Hg}_{0.20} \text{Pb}_{0.45} \).
The 355 K section shows another invariant:

\[ \text{Liq} + \text{hcp}_{\text{Bi,Pb}} = \text{Fcc}(\text{Pb}) + \text{Rhombo…}_A7(\text{Bi}) \]

The isopleth section \( X_{\text{Pb}}/X_{\text{Bi}} = 0.45/0.55 \) (Figure 3.6.3) shows the decrease in liquidus and solidus temperature as the Hg content increases.

**Figure 3.6.1. Isothermal section at 310 K for the ternary Pb-Bi-Hg system [Maître, 2002]**

![Isothermal section at 310 K](image)

**Figure 3.6.2. Isothermal section at 355 K for the ternary Pb-Bi-Hg system [Maître, 2002]**

![Isothermal section at 355 K](image)
3.7 Lead and LBE-water interaction

The increasing interest in heavy liquid metal reactors, based on either lead or lead-bismuth eutectic coolants, raises the question of the effects of their possible interaction with water. The preliminary designs of lead fast reactor (LFR) and of subcritical transmutation systems prototypes, presently foresee the use of steam generation modules in direct contact with the liquid metal of the main vessel. With this configuration an accidental leakage of water into the core vessel cannot be excluded. Moreover, an incidental scenario which could cause a physical interaction between LBE and heavy water has been considered and studied for the MEGAPIE experiment [MSR, Jacobs]. The consequences of such an event must be thoroughly examined due to its impact on the design, the maintenance and the economics of these future reactors.

It should be pointed out that, unlike the cases of sodium or lithium and its alloys, for Pb and PbBi there is no chemical interaction with water and the resulting effects are significantly different.

3.7.1 Literature survey

From a literature review, three main categories of experiments were found:

1) Pb-17Li large-scale experiments [Kottowski, 1991], [Ciampichetti 1, 2003a], [Ciampichetti 2, 2003b];
2) small-scale experiments involving Pb, Pb-17Li, 2Pb7Li and Li [Kranert, 1991];
3) small-scale Pb-Bi experiments [Sibamoto, 2001], [Corradini, 1988], [Nakamura, 1999], [Hibiki, 2000], [Suzuki, 2003].
Large-scale experiments

Large-scale experiments were mainly performed in Ispra and Brasimone with Pb-17Li for fusion applications. Their characteristics are given in Table 3.7.1.

Table 3.7.1. Large-scale experiments

<table>
<thead>
<tr>
<th>Water pressure</th>
<th>Water temperature</th>
<th>Injected mass of water</th>
<th>Liquid metal temperature</th>
<th>Volume of the reaction vessel</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 to 155 bar</td>
<td>225 to 325°C</td>
<td>2.7 to 4.6 kg</td>
<td>350 to 500°C</td>
<td>50 to 100 litres</td>
</tr>
</tbody>
</table>

Due to the chemical and physical interactions, strong and rapid pressure and temperature rises were observed. In some tests, some spikes were detected above the water injection pressure.

LIFUS 5 and BLAST experiments ([Kottowski, 1991], [Ciampichetti 1, 2003a], [Ciampichetti 2, 2003b]) dealt with the interaction between Pb17Li alloy and hot pressurised water coming from large leaks, simulating a cooling tube rupture inside the water-cooled liquid lead-lithium (WCLL) blanket. Due to the production of hydrogen in these experiments, it is not possible to extend the results to the accident scenarios foreseen in lead reactors.

Small-scale experiments

Small-scale experiments made by JRC Ispra [Kranert, 1991], consisted of the injection of water from the top of an expansion tube (d = 9 mm, L = 2 m) into a reaction capsule containing the alloy (d = 24 mm, L = 170 mm) without cover gas buffer. The test conditions are given in Table 3.7.2.

Table 3.7.2. Conditions of small-scale experiments [Kranert, 1991]

<table>
<thead>
<tr>
<th>Water pressure</th>
<th>Water subcooling temperature</th>
<th>Injected mass of water</th>
<th>Liquid metal temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 to 25 bar</td>
<td>10 – 43 – 75°C</td>
<td>1.2 to 200 g</td>
<td>500 to 800°C</td>
</tr>
</tbody>
</table>

The results of the tests carried out with lead and a water injection pressure of 1 bar showed a pressure rise of up to 18 bar due to the coolant column impact on the alloy surface. The 18 bar pressure rise is the highest observed value, excluding the tests with lithium. In fact, an important conclusion of this work was that the chemical reaction between the alloys containing lithium and water inhibits a violent thermo-hydraulic reaction due to the attenuating effect of the hydrogen produced.

A small-scale LBE experiment was performed at JAERI in the frame of reactor safety. The liquid metal was dropped into a water pool having the features shown in Table 3.7.3 [Sibamoto, 2001], [Nakamura, 1999].

Table 3.7.3. Conditions of the JAERI small-scale experiment

<table>
<thead>
<tr>
<th>Water pressure</th>
<th>Water temperature</th>
<th>Liquid metal temperature</th>
<th>Mass of water</th>
<th>Mass of LBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 bar</td>
<td>100°C</td>
<td>250°C</td>
<td>80 g</td>
<td>1.8 kg</td>
</tr>
</tbody>
</table>
These experiments demonstrated that the melt accumulation in the water pool is accompanied by vigorous steam generation at the initial point of contact of the PbBi with water. A violent vapour expansion occurred and was well predicted by a simplified one-dimensional model. The evolution of steam production and expansion was measured by a neutron radiography technique.

For the development and validation of the SIMMER code, [Hibiki, 2000] and [Suzuki, 2003] reported some experimental studies on flow characteristics in gas-molten metal pool. [Corradini, 1988] presents some criteria to predict the conditions for a vapour explosion.

3.7.2 Related risks

The main risk for the structures is associated with the occurrence of a vapour explosion. A vapour explosion is a physical event in which a hot liquid rapidly fragments and transfers its internal energy to a colder, more volatile liquid which in turn vaporises at high pressure and expands, doing work on its surroundings. The vapour explosion criterion advanced by Fauske is based on the comparison between interface temperature and the spontaneous nucleation temperature. For fluids hardly wetting, like water and LBE, the spontaneous nucleation temperature is very close to the homogeneous nucleation temperature which is approximately 310°C for water. This criterion, even if not universally accepted, was confirmed by recent observations collected by [Kurata, 2004] which show that, at 1 atmosphere pressure, a steam explosion is possible over an interface temperature range from about 300°C to the water critical temperature. Other observations by [Kurata, 2004] include:

- Vapour explosion can occur at initial melt temperatures and between about 400°C and 500°C at pressures under 0.1 MPa.
- Vapour explosions seem to occur when the water is sufficiently subcooled, and when the contact temperature is higher than the spontaneous bubble-nucleation temperature.
- Vapour explosions do not occur at pressures above 0.2 MPa.
- Decreasing droplet subcooling diminishes the explosion intensity.

In case where vapour explosions do not occur, the expansion of released water in LBE happens at a slower rate and simpler thermodynamic models can describe the behaviour.

In any case it is advisable that liquid metal/water interaction be studied by means of both experimental and numerical approaches.

3.7.3 Numerical codes

In view of the safety issues related to the severe core melting accident, several numerical codes have been developed in the recent years to assess the effects of the interaction between liquid metals and water. Among these are:

- Mattina;
- SIMMER.

Mattina [Jacobs, 2002] was recently used to simulate a case of LBE-water interaction for the MEGAPIE project. Its limitations are that the code is not suitable for the treatment of film boiling conditions and that the equations of state for lead and lead-bismuth were not originally implemented.
SIMMER is a complex fluid-dynamic code coupled with a neutron kinetics model that has been used to model liquid metal/water interactions [Corradini, 1998], [Hibiki, 2000], [Suzuki, 2003]. The fluid dynamic part is suitable for the modelling of liquid metal/coolant interactions having several different patterns and its data base includes the physical properties of lead and LBE as well.

3.8 Lead or LBE and sodium interaction

There are a number of applications where lead or LBE are used in the same system as sodium. In these cases it is possible for lead or LBE to contact sodium. Such applications include:

- accelerator-driven technology for waste transmutation systems where LBE is used for the spallation target and sodium is used for the transmuter blanket;
- in advanced intermediate heat exchangers (AIHX) for fast breeder reactors in which the secondary liquid sodium is replaced by LBE;
- when a sodium-bonded metallic fuel is deployed inside a LBE cooled blanket.

In all the cases, the consequences of contact between the different liquids under accident conditions have to be considered and evaluated. The information given hereafter is taken from [Crawford, 2001].

Figures 3.8.1 and 3.8.2 show the binary phase diagrams for the Na-Pb and Na-Bi systems respectively [Borgstedt, 1996]. While a ternary Na-Pb-Bi diagram would be more appropriate, the binaries allow an estimate of the potential stable phases for LBE/Na interaction.

These phase diagrams show that Bi is less soluble in Na than Pb but Bi is not insoluble as can be seen from the equation reported by [Walker, 1970].

The Na-Pb compound melting temperatures are around 400°C or less while Na3Bi melts at 840°C.

Moreover, from different studies conducted as part of various programmes, the known products that stemmed from the reaction between Na and Pb or Na and Bi are listed in Table 3.8.1 together with the identified enthalpies of formation. The negative values of the enthalpies of formation indicate that these compounds are stemmed from an exothermic reaction.

**Figure 3.8.1. Na-Pb phase diagram from [Borgstedt, 1996]**

![Na-Pb phase diagram from Borgstedt, 1996](image)
Experimental tests for phase identification consisted of placing measured quantities of Pb or Bi metal onto a measured quantity of solid Na in the bottom of a Petri dish. The metals were then heated in an argon atmosphere from 25°C to a temperature above the melting temperature of Na. Each experiment was terminated after the observed reaction was complete or after the metals had melted and mixed. It has been mentioned “no visible exothermic reaction was noticeable at the melting points of sodium or lead. Once the lead melted, it mixed well with the molten sodium.” [Crawford, 2001]. For the Na-Bi reaction, “A very vigorous exothermic reaction took place at the melting point of sodium. A grey-to-black friable material resulted from the exothermic reaction.” [Crawford, 2001]. The following general observations and/or accomplishments were made as a result of the experimental programme:

1) Investigations and calculations are performed to evaluate the temperature excursion when Na and Bi are put in contact.

2) The Na-Bi reaction is rapid and releases a relatively high amount of heat. The Na-Pb reaction seems less severe but the reason for that is not obvious based on the values of compound formation enthalpies.
3) In the case of a Na cooled transmuter blanket and a LBE target, in analysing the consequences of a blanket-target interface leak, some phenomena must be considered:

a) The Na-Bi and Na-Pb reaction products might plug the leak, stopping the reaction and leading to a benign event.

b) The Na-Bi and Na-Pb reaction products might form in the leak area and stress the target wall, exacerbating the failure and leading to more but this seems not very likely because the material inboard of the target wall would be liquid LBE and there would be nothing solid to maintain the reaction products in a position to stress the original leak area.

c) The Na-Bi and Na-Pb reaction products could be swept away by the flowing Na coolant, where they might dissolve or might simply disperse as solids in the coolant. Looking at the Na-Bi and Na-Pb phase diagrams indicates that the Na-Pb intermetallic is unstable in dilute solutions of Pb in Na, but that the Na\textsubscript{3}Bi intermetallic would be present in dilute solutions of Bi in Na up to temperatures near 600°C. Furthermore, the Na\textsubscript{3}Bi reaction product would likely remain solid at coolant temperatures, whereas the Na\textsubscript{15}Pb\textsubscript{4} reaction product, if at sufficiently high Pb content to remain stable, could precipitate out of Na solution at coolant inlet temperatures. Therefore, it is possible that some reaction products will remain solid in the Na coolant. These products could potentially block flow channels depending on their amount and on their degree of dispersion.

d) If the supply of reacting Na and Bi is not mitigated, significant heat energy from the reaction might be deposited to the blanket or target components but the ability of Na and LBE to dissipate heat and the available volume of Na to absorb the heat would likely prevent such a development.

4) In conclusion, a reaction between sodium and bismuth appears to be sufficiently exothermic that local temperatures could increase substantially, either adversely affecting further reaction, or perhaps introducing reaction products that might block flow channels. Experiments and calculations to assess reaction kinetics and the phenomenology of the reaction in representative conditions of the considered system are needed to well estimate the consequences on the contact between Na and Bi and Pb.

Some experiments have also been conducted by [Saito, 2005] to investigate the reaction between LBE and sodium. They consist in introducing some small amounts of LBE as droplets into a sodium bath. The tests were performed at different temperatures of Na and LBE (between 573 and 673 K) and with various LBE amounts (40 to 140 g as 1-2 mm diameter droplet for 1100 g of Na). The following results were obtained:

- The sodium temperature immediately rises by dropping LBE into liquid sodium due to an exothermic reaction between Na and LBE.
- The reaction between Na and LBE occurs more quickly when the temperature of the melts is high.
- Fine reaction products are formed and they mainly consist in BiNa\textsubscript{3} intermetallic compound. Amount of LBE affects the amount of reaction products and reaction heat.
- The reaction heat deduced from the temperature increase is comparable to the calculated BiNa\textsubscript{3} standard enthalpy value.
3.9 LBE and Pb and organic compounds interaction

The MEGAPIE spallation neutron target uses Diphyl THT (DTHT) oil, produced by Bayer, to cool the LBE target. In the case of a heat exchanger leak, high pressure DTHT will enter the low pressure LBE. Therefore, the consequences of such an event, particularly from a safety point of view, must be evaluated by investigating the chemical and thermal interactions between DTHT and LBE. Therefore, a set of experiments was carried out and is reported in [Leung, 2003]. These experiments consisted of putting DTHT with and without LBE in an autoclave at 350°C under an argon atmosphere.

The results show that:

- No chemical reaction occurs between oil and LBE which induces an increase of temperature and pressure detrimental to MEGAPIE experiment.
- There is a significant difference between apparent gas production rates of the DTHT and DTHT-LBE mixture at elevated temperature. But the net gas production at room temperature was virtually the same in the two cases. This suggests the production of a condensable gas in the experiment with only DTHT.
- There is a lower pressure rise than that which would be expected from the supplier information.
REFERENCES


Ghetta, V., A. Maître, J.C. Gachon (2004), Communication, MEGAPIE.


Chapter 4
CHEMISTRY CONTROL AND MONITORING SYSTEMS*

4.1 Introduction

The development of heavy liquid metal chemistry control and monitoring is one of the issues that is critical for nuclear systems using lead alloys either as a spallation target or as a coolant in the reactor primary circuit of a critical or sub-critical system, from the contamination control point of view as well as from the corrosion point of view.

Corrosion rates at temperatures below 450°C are rather low and satisfactory operation in this temperature range can be achieved using many materials including stainless steels and alloy steels. However, low temperature operation comes at a sacrifice of thermal efficiency, which will have a direct effect on the economics of plant operation for any power producing system. Thus, for applications where economic power generation is the goal, reduced temperature operation is not an acceptable solution. This is especially true for fast reactor systems where capital cost is generally considered higher than that for current light water reactor systems. In the case of ADS and other non-critical systems, however, operation at a temperature for which corrosion becomes acceptable is an option. Low temperature operation does not, however, eliminate the production of spallation and activation products or other contaminants, such as the oxygen or the corrosion products.

Then, for the operation of an HLM nuclear system, the chemistry control and monitoring is a critical issue for at least three distinct requirements:

1) Contamination, the assurance of stable hydrodynamics and heat transfer during service lifetime requires that PbO production be avoided. Lead oxide production may result in plugging due to mass transfer in a non-isothermal system. Also, deposits of other contaminants may eventually reduce the overall heat transfer capacity, etc.

2) Corrosion and/or dissolution must be kept to a minimum to ensure sufficient resistance of the structural materials during the expected service lifetime. This might require the use of active oxygen control to promote and maintain a protective film, although other method could be applied (see Chapter 6).

3) Activation due to corrosion, spallation and fission products might require liquid metal specific control to ensure safe management of the operation and maintenance phases.

The satisfaction of the above requirements makes chemistry control an essential element of nuclear system operation: control of oxygen and other relevant impurities including corrosion products, spallation and activation products. To this end, control processes, in conjunction with monitoring systems, must be developed and/or qualified for application to an ADS system for both the coolant loop (refereeing to the primary circuit), for the spallation target loop and for the primary circuit in any critical system. These issues will be discussed in detail in the following sections.

* Chapter lead: Jean-Louis Courouau (CEA, France).
4.2 Oxygen control in lead and LBE systems

The oxygen is clearly the most important chemical compound for any lead alloy system, because of its potential contamination rate, as well as because of its consequences on the contamination by solid oxides, and its main influence on the corrosion rate of iron-based structures [Shmatko, 2000] [Zrodnikov, 2003] [Martynov, 2003] (see also Chapter 6).

Oxygen comes from the start-up operations, from the maintenance phase as well as possibly from the incidental contamination, for which operating steps the oxygen saturation is more than likely [Courouau, 2003a, 2005a]. To the opposite, its contamination source should be negligible during normal operating mode. If the oxygen concentration must be adjusted to a specified value for corrosion control, the issue of implementing an oxygen contamination source arises. Contrarily, systems for oxygen purification would be necessary for the start up, restart, or maintenance phases. Therefore, the followings points that describe the requirements for operating a nuclear lead alloys system will be detailed hereafter:

1) the upper limit for oxygen to avoid the contamination by coolant oxides;
2) the lower limit for oxygen to enhance the corrosion protection by the self-healing oxide layer, which depends on the structure material – the iron-based alloy will be treated for illustration;
3) the oxygen control policy for nuclear operations, including the method to select the oxygen activity.

Finally, the issue of the homogeneity of the oxygen, which is present in very low concentrations in the lead alloys and submitted to various processes either consuming or releasing it, will be shortly discussed.

4.2.1 Upper limit for the oxygen for operational control

The coolant contamination by its oxides is defined by the solubility of oxygen in lead alloys, giving a maximum allowable oxygen chemical activity in the liquid metal. The following relations define these limits for pure lead and LBE [Gromov, 1998] (see also Chapter 3), for which \( C^*_o \) stands for the dissolved oxygen concentration expressed in weight percentage:

\[
\text{Lead: } \log C^*_o(\text{wt.\%}) = 3.2 - \frac{5000}{T(K)} \quad \text{for } 400^\circ C < T < 700^\circ C \quad (4.1)
\]

\[
\text{LBE: } \log C^*_o(\text{wt.\%}) = 1.2 - \frac{3400}{T(K)} \quad \text{for } 400^\circ C < T < 700^\circ C \quad (4.2)
\]

The accuracy of these relations is not reported, especially for temperature lower than the specified temperature range, although this data is one of the key parameter of the lead alloys chemistry. It will have to be measured more accurately on a wider temperature range, as this relation is commonly extrapolated for the lower temperature. However, it is roughly confirmed by recent verifications [Ghetta, 2004] [Courouau, 2004a] [Ganesan, 2006] (see also Chapter 3).

The main oxide formed in liquid LBE is lead monoxide (PbO), as it is the most stable oxide when compared to other lead oxides and bismuth oxides [Gromov, 1998]. The upper oxygen chemical activity needed to avoid contamination is then defined by the lead monoxide solubility, although in case of a large oxygen contamination, both lead and bismuth oxides will be formed.
In order to calculate dissolved oxygen concentration, the hypothesis of an ideal solution is often made, and the Henry’s law is applied to the dissolved oxygen. Assuming solid lead monoxide as the standard state for the oxygen in lead alloy, the oxygen activity, \( a_o \), shall be equal to unity when saturation is reached [Borgstedt, 1987]:

\[
a_o = \frac{C_o}{C_o^*}
\]

(4.3)

where \( C_o \) is the dissolved oxygen concentration and \( C_o^* \) is the saturated oxygen concentration.

The operating specification to avoid any oxide precipitation in the coolant is then:

\[
a_o \leq 1 \text{ or } C_o \leq C_o^*
\]

(4.4)

This specification must be ensured for all operating temperatures in any point of the loop, both in the liquid bulk as well as at the wall interface.

Table 4.2.1. Oxygen solubilities in lead alloys expressed in \( \mu g/g \) or ppm*

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lead</th>
<th>LBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>130°C</td>
<td>0.01</td>
<td>0.0006</td>
</tr>
<tr>
<td>200°C</td>
<td>0.08</td>
<td>0.01</td>
</tr>
<tr>
<td>330°C</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>400°C</td>
<td>5.4</td>
<td>1.4</td>
</tr>
<tr>
<td>500°C</td>
<td>30</td>
<td>6.3</td>
</tr>
<tr>
<td>600°C</td>
<td>115</td>
<td>20</td>
</tr>
<tr>
<td>700°C</td>
<td>51</td>
<td></td>
</tr>
</tbody>
</table>

* Concentration expressed in weight percentage converts to \( \mu g/g \) (or ppm) by the multiplication by 10^4 or by addition of 4 in the log-type relation.

Table 4.2.1 presents some values for the oxygen solubilities in lead and lead-bismuth eutectic at relevant temperature for a nuclear system operation LBE using Eq. (4.1) and Eq. (4.2) LBE [Gromov, 1998]. As main operating consequence, the safety margin to avoid oxide precipitation is very limited, especially in low temperature range, and its potential risk of circuits clogging is then a real issue. Indeed, any small change in the coolant chemical conditions may induce very quickly oxide precipitation that is not acceptable for a nuclear system.

The upper limit for the oxygen that will be allowed in any non-isothermal system is generally defined by the point where oxide is formed first: the surface of the coldest point because of the thermal gradient between the wall and the liquid bulk, and because oxide can be formed there and thrown elsewhere in the circuits [Shmatko, 2000]. For illustration, if the minimum temperature of the surface of a LBE system is 200°C, the upper oxygen limit for operation would be 0.01 ppm.

### 4.2.2 Lower limit for the oxygen for operational control

Almost all of the elements of significance for structural material development have a lower equilibrium oxygen partial pressure than heavy liquid metal such as lead and bismuth for their oxides. It is then possible, from a theoretical point of view, to promote a protective oxide film by assuring that the oxygen potential in the liquid metal is above the potential for film formation on the structural material for use in the high temperature range (>450°C) (see also Chapter 6). This active oxygen control scheme for corrosion protection has been widely studied for steel structure by the formation of an iron-oxide film (magnetite, \( Fe_3O_4 \)) [Gorynin, 1998]. Russian test data on steels in liquid lead alloy have shown that there exist three different yet distinctive corrosion regimes as function of oxygen concentration. When the oxygen concentration is too low for a stable oxide film, dissolution of metal...
occurs. At high oxygen concentrations rapid oxidation occurs which results in degradation of the structure and/or the formation of Pb oxides. Between these two extremes, there exists a transition region where the kinetics transitions between dissolution and oxidation and the overall reaction rate is kept very small [Ballinger, 2004].

The reliance of an oxide film based on an alloying element of the structure require that the oxygen potential be controlled within a narrow band, the upper oxygen potential being defined by the contamination by Pb oxide, and the lower oxygen potential by the conditions of formation of the protective oxide. The following structural elements are foreseen for corrosion protection by the formation of oxide film, except iron: Cr, Zr, Si, Al [Ballinger, 2004]. ZrO$_2$, Al$_2$O$_3$, SiO$_2$ or SiC can be considered as low solubility materials or be used as barriers layers to limit the corrosion. From the viewpoint of active oxygen control, the lower oxygen limit is firstly determined by the relative thermodynamic stability of the oxide when compared to Pb oxide, the more stable the lower the oxygen potential, and the largest operational temperature range (see also Chapter 3).

First, the stability of various oxides is compared to each other thanks to their free energies of formation (Ellingham diagram). Reactions are written for the consumption of one mole of di-oxygen:

$$\frac{2}{y}Me_{\text{dissolved}} + O_{2\text{dissolved}} \rightarrow \frac{2}{y}Me_{y}O_{y} \tag{4.5}$$

The unit is then expressed in J/mol of oxygen O$_2$. Calculation is made with HSC database software [HSC, V4.1], and the coefficients of the linear regression in the temperature range 400-1000 K, or 127-727°C, are computed to give the standard free enthalpies of formation in the useful operating range, and reported in Table 4.2.2. Indeed, the construction of $\Delta G$ – T diagram is useful to determine the relative areas of stability for one oxide, using the activities product of the previous reaction:

$$\Delta G = RT \cdot \ln P_{O_2} \quad \text{and} \quad \Delta G^o = RT \cdot \ln P_{O_2}^o \tag{4.6}$$

All points of such a $\Delta G$ – T diagram are then meaningful:

- for $\Delta G > \Delta G^o$, the system is outside is equilibrium conditions, and only oxide is present;
- for $\Delta G = \Delta G^o$, the system follows its red-ox equilibrium, where both oxide and the metal are present;
- for $\Delta G < \Delta G^o$, the system is outside its equilibrium conditions, and no oxide is stable.

The corresponding $\Delta G$ – T diagram is plotted in Figure 4.2.1, presenting clearly the more stable and the least stable oxide from a thermodynamic point of view in liquid lead alloy. The isoconcentration lines of dissolved oxygen for respectively 0.01 and 10$^{-10}$ ppm in weight in LBE melt are also plotted for comparison. In particular, it can be noticed that the window for an active oxygen control for corrosion protection by iron oxide film corresponds to the narrow: area delimited by the PbO line (below) and the Fe$_3$O$_4$ line (above). To the opposite, all other potential oxides for other structure candidate materials, SiO$_2$, Cr$_2$O$_3$, Al$_2$O$_3$, and ZrO$_2$ present oxides that will be stable over the whole range of oxygen potential in the liquid metal alloys, including in the higher temperature range.

Figure 4.2.1 is plotted with activity of all impurities equals to unity, meaning that all elements are dissolved in the LBE up to their solubility limit. This is unlikely to happen in nuclear system where impurities from the alloying elements of the structure as well as dissolved oxygen are submitted to mass transfer within the circuits, including release to the liquid metal by corrosion/dissolution of the
Table 4.2.2. Main oxides free enthalpies coefficients for the 400-1000 K temperature range, and for one mole of oxygen computed from [HSC v4.1] (see also Chapter 3)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^\circ$</th>
<th>$\Delta H^\circ$ (400-1000 K)</th>
<th>$\Delta S^\circ$ (400-1000 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{4}{3}$ Al + O$_2$ = $\frac{2}{3}$ Al$_2$O$_3$</td>
<td>-1117.15</td>
<td>-209.8</td>
<td></td>
</tr>
<tr>
<td>$\frac{4}{3}$ Bi + O$_2$ = $\frac{2}{3}$ Bi$_2$O$_3$</td>
<td>-389.14</td>
<td>-192.6</td>
<td></td>
</tr>
<tr>
<td>$\frac{4}{3}$ Cr + O$_2$ = $\frac{2}{3}$ Cr$_2$O$_3$</td>
<td>-755.41</td>
<td>-171.8</td>
<td></td>
</tr>
<tr>
<td>$\frac{4}{3}$ Fe + O$_2$ = $\frac{2}{3}$ Fe$_2$O$_3$</td>
<td>-544.13</td>
<td>-171.2</td>
<td></td>
</tr>
<tr>
<td>$\frac{3}{2}$ Fe + O$_2$ = $\frac{1}{2}$ Fe$_3$O$_4$</td>
<td>-551.99</td>
<td>-156.9</td>
<td></td>
</tr>
<tr>
<td>2 Fe + O$_2$ = 2 FeO</td>
<td>-529.19</td>
<td>-131.4</td>
<td></td>
</tr>
<tr>
<td>2 H$_2$ + O$_2$ = 2 H$_2$O(g)</td>
<td>-490.31</td>
<td>-104.5</td>
<td></td>
</tr>
<tr>
<td>2 Ni + O$_2$ = 2 NiO</td>
<td>-473.69</td>
<td>-175.7</td>
<td></td>
</tr>
<tr>
<td>$\frac{3}{2}$ Pb + O$_2$ = $\frac{1}{2}$ Pb$_3$O$_4$</td>
<td>-357.93</td>
<td>-192.1</td>
<td></td>
</tr>
<tr>
<td>2 Pb + O$_2$ = 2 PbO (litharge &lt; 762 K)</td>
<td>-439.87</td>
<td>-198.8</td>
<td></td>
</tr>
<tr>
<td>2 Pb + O$_2$ = 2 PbO (massicott)</td>
<td>-437.61</td>
<td>-199.1</td>
<td></td>
</tr>
<tr>
<td>Pb + O$_2$ = PbO$_2$</td>
<td>-273.60</td>
<td>-195.5</td>
<td></td>
</tr>
<tr>
<td>Si + O$_2$ = SiO$_2$</td>
<td>-909.32</td>
<td>-179.6</td>
<td></td>
</tr>
<tr>
<td>Zr + O$_2$ = ZrO$_2$</td>
<td>-1094.54</td>
<td>-187.21</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.2.1. Ellingham diagram for lead-bismuth eutectic melt

structure as well as precipitation/oxidation, so the actual activity results from a dynamic equilibrium, which may be very far from unity. Detailed analysis for the iron-based structure is given hereafter for illustration of the methodology used for specifying the lower limit for the oxygen for operational control.
Assuming iron-based alloys and corrosion protection by self-healing oxide layer, the oxygen potential must ensure the conditions for the formation of iron oxide in any part of the system, in the liquid bulk as well as at the wall interface, for all operating conditions. Indeed, the magnetite being the least stable oxide of the layer, it defines the minimum allowable oxygen concentration. The reaction of the steel oxidation in liquid lead alloys is assumed to be as follows:

\[
\frac{1}{4} \text{Fe}^{(\text{dissolved})} + \text{PbO}^{(\text{dissolved})} \rightarrow \frac{1}{4} \text{Fe}_3\text{O}_4 + \text{Pb}^{(\text{liquid})}
\]  

(4.7)

where oxygen is supposed in solution in the form of dissolved PbO under its saturation limit. This is equivalent to consider that a cloud of Pb atoms surrounds the O atom. Dissolved oxygen chemical activity is then referring to dissolved PbO activity. Computed from Table 4.2.1 the standard free enthalpy of reaction is then:

\[
\Delta_r G^\circ (J/mol) = -57190 - 21.1 \cdot T(K) 
\]  

(4.8)

Lead activity is equal to unity in pure lead solution, and is given by the following Russian relation in LBE solution as quoted in [Courouau, 2002b], which is slightly lower than 0.45:

\[
\ln a_{\text{Pb}} = -\frac{135.21}{T(K)} - 0.8598 
\]  

(4.9)

The iron solubility in lead or lead alloys is expressed as [Gromov, 1998] [Tecdoc 1289], and illustrated in Table 4.2.3:

- **Lead:** \(\log C_{\text{Fe( wt.%)}} = 0.34 - \frac{3450}{T(K)}\) for \(330^\circ\text{C} < T < 910^\circ\text{C}\)  
- **LBE:** \(\log C_{\text{Fe( wt.%)}} = 2.01 - \frac{4380}{T(K)}\) for \(550^\circ\text{C} < T < 780^\circ\text{C}\)  

(4.10)  

(4.11)

**Table 4.2.3. Iron solubilities in pure lead and LBE expressed in \(\mu g/g\) (ppm)**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Lead</th>
<th>LBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>130°C</td>
<td>–</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>200°C</td>
<td>0.0006</td>
<td>0.01</td>
</tr>
<tr>
<td>330°C</td>
<td>0.04</td>
<td>0.07</td>
</tr>
<tr>
<td>400°C</td>
<td>0.16</td>
<td>0.3</td>
</tr>
<tr>
<td>500°C</td>
<td>0.75</td>
<td>2.21</td>
</tr>
<tr>
<td>600°C</td>
<td>2.4</td>
<td>10</td>
</tr>
<tr>
<td>700°C</td>
<td>6.2</td>
<td>32</td>
</tr>
</tbody>
</table>

The activity product of the reaction of formation of magnetite in lead alloys is then as follows for equilibrium conditions:

\[
\ln(a_o \cdot a^{3/4}_{\text{Fe}}) = \ln a_{\text{Pb}} + \frac{\Delta_r G^\circ}{RT} 
\]  

(4.12)

Defining the iron activity similarly to the oxygen activity, \(a_{\text{Fe}} = C_{\text{Fe}}/C_{\text{Fe}}^\circ\), it is equal to one when the iron is saturated in the solution, and defining the minimum oxygen concentration required for effective corrosion protection, \(C_{o,min}\) (in wt.%), the following relations are derived:
Lead: \( \log C_{O_{min}}(\%) = -\frac{3}{4} \log C_{Fe}(\%) + 2.355 - \frac{10600}{T(K)} \) (4.13)

LBE: \( \log C_{O_{min}}(\%) = -\frac{3}{4} \log C_{Fe}(\%) + 1.2375 - \frac{9757}{T(K)} \) (4.14)

If the system enters the dissolution area, and if in situ oxide layers protect the structure, there will be a certain time lag corresponding to the time required to dissolve the magnetite and spinel oxide layers. This somehow introduces a safety margin. Conversely, when going back to the right oxygen level, there will be some delay. During these periods, the only measurement of oxygen is not enough, as oxygen concentration will be kept steady, defined by the iron oxide chemical reaction equilibrium. This is analogous to a buffer effect. The only way to detect if the oxide layer is dissolving or growing would be to measure directly its thickness using an electrical resistance probe measurement [Provorov, 2003].

The lower limit for the oxygen that will be allowed in any non-isothermal system is generally defined by the point where the iron oxide will be dissolved first: the surface of the hottest point because of the thermal gradient between the wall and the liquid bulk. For illustration, if the maximum temperature of the surface of a LBE system operating with a structure made of iron based alloy is 650°C (hot spots), the lower oxygen limit for ensuring the iron oxide formation would be about 0.0005 ppm.

4.2.3 Specifications for active oxygen control

The oxygen concentration areas of operation to ensure both no contamination, required for any system, and possibly corrosion protection for higher operating temperature are similar for the liquid lead or the lead-bismuth eutectic:

\[ C_{O_{min}} \leq C_O \leq C'_O \] (4.15)

The operating specifications for oxygen is evaluated from the Figure 4.2.2 drawn with the previous relations illustrated for active control for iron-based structure, knowing that for other non-ferrous structure materials, the specification for active oxygen control for corrosion protection would be less restrictive.

The minimum oxygen concentration required to ensure the oxide layer stability is plotted against the saturated iron content, which maximises the oxidation area as for lower iron concentration the minimum oxygen concentration increases (Figure 4.2.2) [Gromov, 1998] [Shmatko, 2000]. For an isothermal system, a vertical line plotted at the system temperature defines the oxygen range that is allowed: as illustrated in Figure 4.2.2, a system operating at 420°C is giving an oxygen range of 2.5 \( 10^{-6} \) to 2 wt-ppm. In principle, for a non-isothermal system, the intersection of the two ranges defined by the vertical lines plotted respectively for the cold and the hot legs temperatures are defining the oxygen range. As illustrated in Figure 4.2.2, a system operating between 420°C and 540°C would then give an oxygen range of 6 \( 10^{-5} \) to 2 wt-ppm.

For non-isothermal systems, the temperature at the interface is different from the bulk temperature because of the heat transfer process. However, if the oxide layer protection is required, the minimum oxygen content must be ensured at the wall temperature, which defines the oxygen concentration range allowed for operation for a given system. For instance, in the BREST-300 like coolant, the
operating conditions are: operating coolant temperature 420-540°C, maximum fuel clad temperature of 650°C (hot spots), and minimum steam generator wall temperature of 200°C [Shmatko, 2000]. Thus, the oxygen concentration must be kept lower than 0.01 wt-ppm to prevent coolant oxidation at 200°C and higher than 0.0005 wt-ppm to keep oxide protection at 650°C for saturated iron activity (αFe = 1), that could be compared to the range defined only by the bulk temperatures: 6 \times 10^{-5} \text{ wt-ppm (420°C)} to 2 \text{ wt-ppm (540°C)} which is drastically larger. If the same kind of conditions are required for lead coolant, the range of oxygen to ensure no contamination and corrosion protection by iron oxide is 0.31 wt-ppm at 375°C and 2 \times 10^{-3} \text{ wt-ppm at 650°C, which is even narrower} [Courouau, 2004b].

\textbf{Figure 4.2.2. Oxygen specifications in LBE}

\emph{For a BREST-300 like primary coolant, showing in shaded area the allowable oxygen operating range, as well as the contamination (C_{o}=C_{o}^{s}), the oxidation (C_{o}\text{min} < C_{o} < C_{o}^{s}) and the dissolution (C_{o} < C_{o}\text{min}) areas.}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{oxygen_specs.png}
\caption{Oxygen specifications in LBE}
\end{figure}

However, the condition that iron is present in saturated condition is foreseeable in static condition, but unlikely in dynamic loop condition where mass transfer will play a role. Indeed, in a non-isothermal system, the iron will be released from the hot structural wall by corrosion, and transferred to locations with lower temperature, where it may precipitate. The diffusion and the convection processes are the 2 mechanisms responsible for the mass transfer: usually, the diffusion of the species from the wall to the liquid bulk through the boundary layer is the limiting process. This latter includes the diffusion through the oxide layer when it is present. The thermodynamic condition for oxide formation on the interface can then be quite different from the condition in the liquid bulk, which is the result of a dynamic equilibrium (\alphaFe < 1). Figure 4.2.3 illustrates this: decreasing the iron concentration reduces the oxidation area, the higher the temperature the higher the reduction. For working at higher temperature, the oxygen content should then be close to its saturation limit. Indeed, the iron in equilibrium with its oxide at the wall interface can then be several orders of magnitude lower than its solubility, which reduces in turn the corrosion rate to low or very low level. This is the working mechanism behind the active oxygen control and the oxide film formation [Gromov, 1998] [Shmatko, 2000] [Li, 2002], which was recently more fully investigated from a theoretical point of view [Martinelli, 2005].

It can be noticed that the higher the operating temperature and the smaller the oxidation area, which will eventually prevent the use of active oxygen control for corrosion control by iron oxide film formation in the high operating temperature range (around 700°C).
Figure 4.2.3. Iron oxide formation threshold defining the couple of solution to ensure a protective oxide layer depending on both the iron ($C_{Fe}$ or $c$) and oxygen concentrations ($C_{o}$), in LBE expressed in wt.% and ppm respectively for the left and the right hand side graph.

The iron concentration is difficult to measure and impossible to monitor on-line up to now. The lower detection limit is 5 wt-ppm by chemical analysis up to now, and could possibly be lowered to 0.5 wt-ppm, which may still be higher than the iron concentration expected. There is no straightforward solution to control the iron content, but oxygen should be controlled and monitored on-line so that it gives at least the hand on one parameter. As a consequence, the oxygen specification should be set at the highest possible value that complies with the contamination requirement, which corresponds to the cold leg temperature interface, as this is maximising the oxidation area for an unknown iron concentration, which is defining the specification for oxygen control:

$$C_{o}\left(\frac{Contamination}{and\ corrosion\ control}\right) = C_{o}^{*}(cold\ leg\ wall\ temperature) \quad (4.16)$$

From the previous example, the oxygen concentration specification chosen would then be 0.01 wt-ppm.

This thermodynamic analysis was made thanks to some assumptions, and could be more or less well applied to perlite steel ($Fe\ 100\%$), but might be slightly different for Cr alloyed steel or even, Zr, Si, or Al based materials or corrosion barrier materials, as the oxide layer will be a compound of more stable oxides. Real operating limits should be measured on test facilities in representative operating conditions and for relevant materials.

### 4.2.4 Policy for a nuclear system

The oxygen control is then a basic requirement for nuclear relevant system, for which long service lifetime is expected, meaning interventions for components and fuel handling, repair and maintenance, requiring a purification of the oxygen before any restart, together with a requirement for a as high as possible operating temperature, which might require the corrosion control by self-healing oxides layer on the structural iron-based materials.

The contamination represents the main issue during the initial operations (first filling, start-up...) [Ivanov, 2003a] [Courouau, 2004c, 2005a], as well as during the maintenance and repair phases: air ingress can happen and the oxygen is released from the structural materials as well as from the LBE itself. It is critical to ensure that the liquid metal is kept clean and that no solid oxides are formed, as
these could possibly clog narrow sections of the facility, or deposit on heat exchanger surface, so that the overall cooling capacity of the system can be affected. However, it is reported [Martynov, 2005], and usually well observed, that there are no difficulties during the start-up of facilities from the viewpoint of the coolant purity and cleanliness, meaning that a few percent of solid lead oxide in the liquid metal melt appears still compatible with flowing conditions. However, the accumulation the long-term operation of the oxide, if not treated regularly, will eventually hinder the operation of the facilities by affecting its cooling capacity (clogging, deposits on pipes). Amount of solid oxide and deposit in circuits were recorded up to 5% of the coolant mass in the circuit [Martynov, 2005]. These deposits are composed of mainly PbO and LBE, with traces of iron, and are not affected by high temperature or by low oxygen concentration. Such occurrence of a two-phase flow is not acceptable for nuclear operation, so that the contamination must first be reduced to the minimum, as well as systems for regular purification must be implemented [Martynov, 2005].

Known major oxide slag formation failures date back from the 60s: the initial run of the KV/27 land nuclear reactor based at IPPE and the project 645 nuclear submarine failure on cruise [Ivanov, 2003b]. For the latter, a sudden ingress of slag in the core during sea trials in 1968 caused a loss of power by negative temperature reactivity effect. The crew tried to restore the power by levelling off the control rods that led to partial melting of the core. In fact, there were at least two sources of contamination for the coolant: the oxygen accumulated during the maintenance phases and the oil contamination from the rotating shaft of the primary pumps. As there were no quality-monitoring devices, nor process for purification, the slow ongoing contamination and accumulation could not be detected nor treated, eventually leading the nuclear failure of the system.

By contrast, during the normal operating mode, the oxygen contamination sources are then negligible, so that, because of the various source of consumption of the oxygen, one can expect low or very low oxygen content in the liquid metal loop [Shmatko, 2000]. The corrosion control by active oxygen control could then be critical during that operating period, depending on the choice of the materials, and of the operating temperatures. For iron-based alloys and for temperature higher than 450°C, for which the corrosion rates by dissolution become not more negligible, the active oxygen control would be required. The use of other materials, such as low solubility materials such as composite SiC, ceramic Al₂O₃, ZrO₂ that presents low solubility in lead alloys, or applied on a substrate materials as a barriers layers [Ballinger, 2004], may present a so large area of use as regard the oxygen that the lower oxygen limit may not be achievable in practice, excluding any requirement for active oxygen control.

The requirements for oxygen control systems could then be divided into:

1) purification from oxygen during start-up, or restart to prevent the formation of lead monoxide;
2) active oxygen control for corrosion protection during the normal operating mode, and possibly at the initial stage to promote the formation of a protective oxide layer.

The first requirement consists in ensuring the contamination control in any part of the circuit and for any operating condition, in order to avoid the oxides formation of firstly the coolant oxides. This requirement is common to all nuclear systems.

The second requirement consists in active oxygen control for promoting a protective oxide film formation on the structure by controlling the oxygen potential in the liquid metal. This requirement depends on the design specifications of the systems, and firstly its operating temperatures, and then on the choice of the materials.
If no corrosion control is required, the contamination specifies the upper threshold for the oxygen control as follows:

\[ C_\text{ontamination control only} \leq C^\circ\text{(cold leg wall temperature)} \quad (4.17) \]

This choice was made for the MEGAPIE target, thanks to the choice of low operating temperature (\(<400^\circ\text{C peaks}\)) for the short service lifetime (6 months). Figure 4.2.4 represents the expected oxygen concentration during its service lifetime, from its start-up tests to the on-beam operations. Its service lifetime was assessed as compliant with the corrosion by dissolution of the steel at the low operating temperature chosen. However, Figure 4.2.4 clearly indicates that the conditions for dissolution would be achieved after a certain delay, necessary for the residual oxygen present in the liquid bulk as well as the residual oxide layer present on the steels to dissolve, which may takes weeks or months depending on the initial oxide layer and the production of hydrogen and spallation products. This time lag will limit the overall corrosion further on.

Figure 4.2.4. Oxygen expected behaviour for the MEGAPIE target during start-up operation (integral test stand – MITS), and during beam steady state operation where the oxygen will be reduced first down to the iron oxide stability threshold, and then even further down when all iron oxide will be reduced after an certain delay [Courouau, 2005a]

4.2.5 Oxygen control systems

The first requirement consists in ensuring the contamination control in any part of the circuit and for any operating condition, in order to avoid the oxides formation of firstly the coolant oxides. This requirement is common to all nuclear systems.

For any nuclear lead alloys circuits, it is necessary to provide the following systems for the oxygen control:

- oxygen measurement systems for on-line monitoring for the cover gas and the liquid metal;
- oxygen control systems for purification, and possibly for active oxygen control.

Indeed, the oxygen will behave accordingly between the cover gas and the liquid phase in normal operating condition, where equilibrium will be reached most certainly. As the main contamination sources are not part of normal operation, it is important to be able to detect the transient due to
contamination as soon as possible. As the transient could be very different from one phase to another, because of the large difference in volume, the oxygen measurement in both media is required. This was the main lesson learnt from the 1990 air contamination at SUPERPHENIX, where only liquid metal quality sensor was implemented, although the plugging-meters were actually indicating the occurrence of the contamination, but the correct interpretation was not done. Since then on, as it was already performed on PHENIX since the beginning, gas chromatography of the cover gas allows detecting any variation of nitrogen content that will allow detecting any air ingress quickly, as the oxygen reacts quickly with sodium.

The oxygen monitoring system for the liquid metal bulk, also referred to as the oxygen sensor, is part of a complete development in itself and will be detailed hereafter in a specific section. Measuring devices for the oxygen in the gas phase are commercially available.

The oxygen control processes will be briefly detailed hereafter.

Processes for the oxygen control in lead-bismuth systems are basically of two different kinds:

- gas phase control;
- solid phase control.

The principle of the gas phase control is based on gas/liquid equilibrium between the cover gas and the liquid bulk when the liquid is below saturation. Controlling the oxygen partial pressure in the gas phase would set the dissolved oxygen content.

In practice, pure oxygen or hydrogen are flowed in the cover gas, usually in dilution with argon, which is easy to achieve over flowing liquid in vessel, provided the interface is well mixed, or directly with the help of a bubbling line for a larger exchange area, in order to oxidise or reduce the liquid lead alloys according to the following reactions:

\[
Pb_{(\text{liquid})} + O_{2(\text{gas})} \rightleftharpoons PbO_{(\text{dissolved})} \tag{4.18}
\]

\[
PbO_{(\text{dissolved})} + H_{2(\text{Gas})} \rightleftharpoons H_2O + Pb_{(\text{liquid})} \tag{4.19}
\]

The use of hydrogen gas allows recovering from oxides accumulation after a large contamination, for star-up or maintenance, or after prolonged operations in order to restore the thermal-hydraulic performances of the system. The mechanical impact of bubbles is reported to increase the efficiency of the process by putting back into solutions particles of deposit, which should be used together with a filtration system [Papovyants, 1998]. The use of getter addition, such as Zr, or Mg, will reduce the oxygen to the low concentration but will produce other solid oxides at the same time that would have to be purified somehow. Hydrogen presents the main advantages to produce only a gaseous reaction product that is easily evacuated in practice through the vent line.

However, it is not easy to achieve the very low oxygen potential that is required for active oxygen control in the cover gas, so that the use of a ternary gaseous mixture is more practicable. Indeed, by fixing the ratio of steam over hydrogen for instance, the oxygen potential in the liquid metal is determined by the thermodynamic equilibrium [Gulevski, 1998], [Mueller, 2000], [Shmatko, 2000]. In principle, the use of other reaction system could be used, such as the CO/CO\textsubscript{2} system, but are not favoured for practical and safety reason. This can be used for the purification processes of system where oxide film is protecting the structure, in order to protect the oxide film from dissolution [Martynov, 2005]. Moreover, the use of a CO/CO\textsubscript{2} system should be evaluated with a special focus on the potential carburisation effects on the structural material.
The process parameters of the gaseous systems are related to the mass exchange at the gas-liquid interface that limits the equilibrium process in practice. Bubbling, which increases the exchange area greatly, favours the exchange, and then the time to reach the thermodynamic equilibrium. Temperature is the second main parameter for the hydrogen reduction of solid lead oxide [Ricapito, 2002], the higher the better, which might be related to the solubility. To the opposite, the oxidation is fast, which may lead to solid oxide formation rather than dissolved oxygen, which can be transferred and settled in other part of the facility, and then requiring subsequent purification. This is why oxidation at a slower rate is better achieved when adjusting directly the gas phase composition with the help of a ternary gas mixture.

To avoid the oxidation in excess and the solid oxide formation within the system, solid mass exchange was proposed [Gromov, 1996], [Zrodnikov, 2003]. It consists in dissolving solid lead oxide, which physical form is mechanically stable such as in pellet (Figure 4.2.5), in a device where the thermal-hydraulics is controlled. Indeed, the dissolution rate is depending on temperature and flow rate [Askhadulline, 2003, 2005], [Simakov, 2003], which give rise for the automated control of the oxygen by adjusting the consumption due to the oxidation with the contamination rate delivered to the system. The solid mass exchanger unit can be designed as a consumable item or for the whole service lifetime of small device such as spallation target, avoiding the handling requirement. Such a system will spare the needs for a complex gas circuits to be operated in a nuclear environment, except probably a regular venting out of the spallation residues, thus enhancing the confinement and the overall safety of the system.

**Figure 4.2.5. Lead monoxide pellets device for oxygen supply to the coolant using the solid phase method [Martynov, 2003], [Askhadulline, 2005]**

\[
(G - \text{liquid flow rate})
\]

4.2.6 The oxygen homogeneity issue

Considering the oxygen as perfectly homogenised within the circuit [Shmatko, 2000], [Orlov 2005], i.e. that there is no limitation to the mass transfer because of the little convection/diffusion rate of the dissolved oxygen within the liquid metal, the oxygen concentration would be constant over the whole system. However, the condition for oxygen homogeneity is questionable. In the case of the corrosion protection, the oxygen range will be rather low, so that the process will only be qualified if the oxygen behaviour is controlled over all part of the circuits for all operating conditions. This means no lower oxygen spots where corrosion could happen, nor higher oxygen spots where Pb oxide can built up. This depends on the various convection and diffusion data for oxygen in lead alloys system (see also
Chapter 3), which are known as rather limited [Zrodnikov, 2003]. However, the low oxygen diffusivity in lead alloys could be, somehow, compensated for by higher convection in the system, ensuring the vigorous stirring of the liquid metal, and then its homogeneity.

In small scale systems, such as SVBR-75 [Toshinsky, 2000] or the Angstrem concepts [Tecdoc 1056], the liquid is renewed hundreds of times per hours, as illustrated in Table 4.2.4, so that the liquid phase can be assumed as perfectly stirred and homogeneous. In addition, as the volume of the coolant is small, there should be no stagnation zones. However, the highest flow velocity does not exceed 2 m/s on the fuel-cladding walls. For larger system the homogeneity might not be ensured, especially because of the lower convection. For instance, the pool-type liquid metal reactors, such as BREST or sodium-cooled reactors, the system mass change rates are 10 times lower than for the small-scale reactors (Table 4.2.4), primarily because these reactors hold considerably larger coolant volume. Dealing with the system mass change rate, the circulation loop-type reactor, when compared to pool-type, would be more efficient from the homogeneity point of view. Even though it would be necessary to compare in much more details distribution of Reynolds number in various parts of the reactors. The main event that can modify the distribution of impurities throughout the reactor (loop or pool type) is the shutdown or isothermal stand-by, which may affect the impurity distribution between hot plenum and cold plenum.

Table 4.2.4. Typical design parameters for core coolant circulation for various reactors

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Core flow rate</th>
<th>Primary coolant</th>
<th>System mass change rate</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHENIX – 350 MWe (Na)</td>
<td>10260 t/h (3 * 0.95 t/s)</td>
<td>840 t</td>
<td>12 times/h</td>
<td>400-550°C (150°C)</td>
</tr>
<tr>
<td>SUPERPHENIX – 1500 MWe (Na)</td>
<td>61056 t/h (4 * 4.24 t/s)</td>
<td>3250 t</td>
<td>19 times/h</td>
<td>395-545°C (150°C)</td>
</tr>
<tr>
<td>EFR – 1470 MWe (Na)</td>
<td>61170 t/h</td>
<td>2100 t</td>
<td>29 times/h</td>
<td>395-545°C (150°C)</td>
</tr>
<tr>
<td>PWR – 1300 MWe (light water)</td>
<td>68000 t/h</td>
<td>380 m³</td>
<td>179 times/h</td>
<td>286-323°C (37°C)</td>
</tr>
<tr>
<td>SVBR – 75 MWe (EPB)</td>
<td>3492 m³/h (11.18 t/s)</td>
<td>18 m³</td>
<td>194 times/h</td>
<td>275-439°C (164°C)</td>
</tr>
<tr>
<td>NPHP Angstrem – 30 t (EPB)</td>
<td>382 m³/h</td>
<td>3 m³</td>
<td>127 times/h</td>
<td>280-465°C (185°C)</td>
</tr>
<tr>
<td>BREST – 300 MWe (Pb)</td>
<td>143640 t/h (3.8 m³/s)</td>
<td>600 m³ (6300 t)</td>
<td>23 times/h</td>
<td>420-540°C (120°C)</td>
</tr>
<tr>
<td>BREST – 1200 MWe (Pb)</td>
<td>570240 t/h (158.4 t/s)</td>
<td>2500 m³ (26250 t)</td>
<td>22 times/h</td>
<td>420-540°C (120°C)</td>
</tr>
</tbody>
</table>

The recommendation from [Shmatko, 2000] is to provide at the circuit design stage provisions to avoid any perturbation of the flow (junction, abrupt turns, etc.), and to exclude any stagnation zones. This would in principle limit the contamination, accumulation, and potential rapid release due to thermo-hydraulic instability such as during hot stand-by and shutdown of the reactor.

However, the only possibility to validate a design for the safety authorities as regards the corrosion protection by self-healing oxide would be to model the mass transfer within the system, using accurate data on convection and diffusion of impurities, and appropriate relation to represent the corrosion/precipitation phenomena in circuits [Zrodnikov, 2003], [Balbaud, 2001], [Li, 2002].
4.3 Characterisation of impurities and requirements for control

4.3.1 Impurity sources

One of the main, and most important, impurities is oxygen. However, there are other sources of contamination that could present some macroscopic effects on the operation even though occurring at a microscopic rate.

Apart from oxygen, the other main contamination sources include: (1) corrosion products (Fe mainly, Ni, Cr, etc.) expected to be generated continuously at a rate depending on the operating temperature, liquid metal flow rate, etc., (2) activation products from spallation, corrosion product activation, or fission (Po, Hg, Tl, Cs, Mn, ...) and (3) light particle production such as hydrogen (including tritium) within the reactor core, the sub-critical assembly or the spallation target.

In addition, if a self healing iron oxide film corrosion protection method is applied for iron based alloys, the oxygen must be controlled within a very narrow range, above the Fe$_3$O$_4$ formation potential but below the PbO formation potential (see Section 4.2.3). Advanced alloy systems that rely on either Si or Al based oxide formation for protection will expand the acceptable oxygen potential range. However, the effect of impurities, whether from the corrosion process itself, or due to contaminants introduced by other means can have a significant effect on the oxygen level required for protection, especially during transient phenomena, such as reactor hot or cold shutdown, which may affect dramatically the impurity distribution and stability within the liquid metal system. For this reason it is important that a complete determination of the potential impurities/contaminants be identified and characterised.

The sources of impurities can be listed by analysing the reactor system conditions during various operating modes including: (1) initial start-up before the first irradiation, (2) normal operating conditions, including start-up and shutdown; and, (3) transient & accidental conditions. Table 4.3.1 gives a synthesis of the various contamination sources expected for an accelerator driven system [Tecdoc 687&1289] [Courouau, 2003a, 2004b].

During normal operation, the only sources of contamination for an ADS system (primary circuit) will then be hydrogen and transition metal or metalloid impurities coming either from corrosion in the whole circuit or from spallation reactions in the target. An additional and incidental source of radio-contamination of a critical system would be from any failed fuel cladding.

A potential source of hydrogen in the intermediate circuits comes from the permeation from the steam generator units, if the energy conversion is performed with a Rankine cycle with steam, because of the steel aqueous corrosion as well as the thermal decomposition of the hydrazine (N$_2$H$_4$) added (in excess to the dissolved oxygen) in the water/steam circuits for reducing the aqueous corrosion. Actual diffusion rate will depend on the hydrogen partial pressure difference as well as on the oxide film thickness at the liquid lead alloys interface, of the steam-generator unit.

Another source of residual hydrogen would be from the proton beam in the spallation target and light element production by ternary fission that includes tritium. It can also be mentioned the degassing of hydrogen adsorbed during some fuel elaboration process, which is almost negligible.

For an ADS system, protons from the beam itself represent an intrinsic hydrogen source, as not all the protons injected into the system will result in a spallation reaction: unused protons will be thermalised and dissolved into the liquid metal as ionic hydrogen. The residual amount of hydrogen is however not well known. Spallation reactions generate hydrogen as well, in quantities that have been roughly assessed for instance for the MEGAPIE experiment to several litres of hydrogen, including
about 10% of tritium (69 l of LBE, 200 days of irradiation, 1.74 mA), which order of magnitude is not negligible, especially since the amount is steadily increasing with the irradiation time that could give rise to an accumulation effect in the spallation target, even though part of it reacts with oxides films or adsorbed gases.

Table 4.3.1. Typical impurities sources in nuclear HLM systems

<table>
<thead>
<tr>
<th>Pollutions sources</th>
<th>A</th>
<th>B</th>
<th>Species</th>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cover gas renewal</td>
<td>x</td>
<td>x</td>
<td>O; H₂O</td>
<td>Negligible</td>
</tr>
<tr>
<td>Steam leak from SG</td>
<td>x</td>
<td></td>
<td>H₂O, (O, H)</td>
<td>Major if microleak or tube rupture</td>
</tr>
<tr>
<td>Spallation residues, ternary fission and proton beam</td>
<td>x</td>
<td></td>
<td>Po, Hg, Tl, Au, Os and Ir</td>
<td>Release to the environment</td>
</tr>
<tr>
<td>Fuel/fuel cladding</td>
<td>x</td>
<td></td>
<td>⁵⁴Mn, ⁵¹Cr, ⁵⁹Ni, ⁵⁶Co, ⁶⁰Co, ¹¹⁰mAg-110m</td>
<td>Coolant activation</td>
</tr>
<tr>
<td>Corrosion products</td>
<td>x</td>
<td>x</td>
<td>Fe, Cr, Ni</td>
<td>Plugging/deposits</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>x</td>
<td>x</td>
<td>O</td>
<td>Plugging/deposits</td>
</tr>
<tr>
<td>Intrinsic pollution</td>
<td>x</td>
<td>x</td>
<td>Ag, Cu, Sn, …</td>
<td>Grade definition</td>
</tr>
<tr>
<td>Gas adsorption in structures during maintenance</td>
<td>x</td>
<td></td>
<td>O; H₂O</td>
<td>Plugging/deposits</td>
</tr>
<tr>
<td>Air inlet</td>
<td>x</td>
<td></td>
<td>O; H₂O</td>
<td>Plugging/deposits</td>
</tr>
<tr>
<td>Fuel cladding failure</td>
<td>x</td>
<td></td>
<td>²³⁹Pu, ²³⁵U, ⁸⁵Kr, minor actinides and Cs, I, Kr, Xe nuclides</td>
<td>Activation on the long term</td>
</tr>
<tr>
<td>Air ingress</td>
<td>x</td>
<td>x</td>
<td>O; H₂O</td>
<td>Plugging/deposits</td>
</tr>
<tr>
<td>Steam ingress</td>
<td>x</td>
<td></td>
<td>H₂O</td>
<td>Cover gas pressurisation, plugging/deposits</td>
</tr>
<tr>
<td>Casual pollution (oil, Hg, …)</td>
<td>x</td>
<td></td>
<td>Oil, Hg, Pb-Sn, …</td>
<td>Plugging/deposits</td>
</tr>
</tbody>
</table>

The ternary fissions have to be accounted for, as it is usually not negligible. Production depends from the ternary fission yields for ²³⁹Pu, ²³⁵U and ²³⁸U. This produces all of the hydrogen nuclides continuously but at low rates, which is usually not negligible for the tritium with regards to the contamination release issue. As this impurity is produced inside the fuel rod, diffusion toward liquid metal is function of the fuel-cladding material, its operating temperature, and of the surface state of the material in contact with the liquid metal: steel retains almost no hydrogen or tritium, whereas zirconium alloys retains all hydrogen. Real transfer rate would have to be assessed for HLM systems, especially if specific coating (alumina) or surface modification treatment (GESA) is used, as it can significantly reduce the share of the contamination effectively transferred to the liquid media. In addition, if the use of neutron absorbers such as boron carbide is foreseen, its contribution to the tritium source would have to be accounted for, as its share might not be negligible when compared to the ternary fission contribution [Courouau, 2003a].

The steam generator units, if any, are normally designed as leak proof. However, some micro leaks could be expected, either because of the lower detection limit of the leak detection system, or because of some tolerance agreed for operation (a few litres/hours). From the liquid sodium reactor experience, a null leak rate between water-steam circuit and the secondary sodium circuit is, however, achievable, with extra constraints on the nuclear operation for the leak detection system and steam generator design. From the Russian experience [Toshinsky, 2000] [Shmatko, 2000], operation with small leaks is reported for some time without significant deviation of the designed technological parameters, which allowed the repair to be done at a convenient time. Indeed, the actual rate of oxidation in case of a small steam leak appears as limited [Shmatko, 2000] and does not induce the
formation of solid lead oxide in excess, but rather to a dynamic equilibrium in the intermediate oxygen range [Martynov, 2003]. This observation gives rise to the principle of direct contact steam generator [Martynov, 2003, 2005], as well as to the concept of Pb-Bi cooled direct contact boiling water small fast reactor (PBWR) [Takahashi, 2003]. The accurate knowledge of the possible micro leak rate is critical, as if any, it will most probably exceed all other contamination rates in oxygen. The relation giving the oxidation of lead by water is given in [Martynov, 2005]: oxidation stops once the oxygen activity reaches $10^{-3}$ of its saturation limits. The potential impact of larger leaks relates to the pressurisation of the cover gas.

The other initial contamination consists in the residual compounds in lead or LBE after manufacturing: it is not the most important one, but represents a source that can be easily dealt with, either by the choice of a “nuclear grade” lead or lead alloy (see Chapter 3), or by the application of specific procedures that would enable to start the nuclear operation with the lowest impurities level achievable.

During the initial start-up, or any restart after maintenance or repair, the oxygen is clearly the largest contamination at this stage of the operation of the nuclear facility [Ivanov, 2003b], [Courouau, 2004c, 2005a]: chemical control and monitoring will enable to control the chemistry of the lead alloys prior to its first irradiation, as well as prior to any operating cycle. Moist air is adsorbed on the residual lead alloys layer as well as on the structural steels in a comparatively high amount that will have to be purified before any restart of the system. This contamination source that was neglected for the first submarine named “project 645”, as it was not known, led to the gradual accumulation of oxide in the primary circuit, which eventually concluded, together with the chronic oil leakages of the pumps, to the on-sea accident in 1968 [Ivanov, 2003b]. This accident occurred a few months after the second core have been loaded, and is at the origin of the intensive studies undergone by the Russian related to the liquid lead alloys technology control in the 70s.

The evaluation of the release rates of corrosion products to the liquid metal is rather difficult as it depends firstly on the choice of materials (iron-based steels, ceramics, refractory metals…), on the corrosion mechanisms as well as on the corrosion protection policy chosen (none, self-oxide healing for steels, coating), on the oxygen activity, on the structural materials and on the operating conditions (see Chapter 6). However, the order of magnitude for iron, chromium and nickel for the coolant loop account to a few kilograms per year when iron-based steels would be used for a primary circuit of significant size. This impurities source is then not negligible over years of operations, and should be accounted for, even though it is only roughly assessed for the moment, and variations in the estimations could be very large.

4.3.2 Behaviour of impurities and requirements for purification

As previously listed, most of the contamination by impurities can be expected to remain limited in mass, except for oxygen and corrosion residues. Corrosion products potentially present long-term and cumulative effects, mainly because of the dynamic mass transfer equilibrium that will occur in a non-isothermal system. Pipes clogging due to corrosion products were experienced in several loops which is a specific issue of the HLM: hot or cold stand-by may lead to a rapid redistribution of the deposited impurities within a few hours, eventually clogging the cold pipes as it was observed on the CICLAD loop (see Chapter 12) as illustrated on Figure 4.3.1. This effect was observed within a few hours, as impurities were first accumulated in some cold spot within the loop, then following a change in the loop temperature distribution, the pump duct became the lowest temperature spot in the loop and got plugged. Such observations are reported for almost all research facilities operating with lead alloys and would not be acceptable for any nuclear system.
The noble elements, whose oxide are less stable than the lead monoxide, will be dissolved in the liquid metal melt up to their solubility limit, and then be present probably as particles (see Chapter 3). In addition, depending on the level of oxygen controlled in the facility, the impurities might be present either in the oxide or dissolved form according to the Ellingham diagram. In any case, mass transfer from the hot part to the cold part, as well as from the liquid metal bulk to the walls, will occur, thus generating an operating risk for long term operation, so that it is required to propose a continuous purification process to control these continuous contamination sources.

**Purification requirements**

For a lead-alloy coolant system, which is foreseen to operate for 30 years or longer, as well as for target loop systems, which, due to operating conditions, are expected to be operated only a few years, it appears necessary to trap continuously the impurities in a specific unit. Specific purification campaign during isothermal stand-by and cold shutdown should be foreseen as well.

In principle, only the solid impurities, insoluble particles or oxides should be gathered in a bypass line containing precipitation, filtration,… capabilities. Lower operating temperature will allow minimising the amount of dissolved species. In addition, temperature gradients or packing may promote efficiently crystallisation of these metals and increase the efficiency of the purification unit.

As some homogeneous crystallisation might happens, then, the conditions to provide enough sedimentation and residence time for the existing particles in a cold quasi-stagnant auxiliary vessel should be investigated as an alternative purification system for some specific needs, for example start up purification prior the filling operation. Particles could then be skimmed off from the gas-liquid interface, as most probably some will be settled up at the interface. This interface could be arranged in specific unit, rather than in the loop, as this will affect the gas-liquid equilibrium with non-metallic impurities (O, H…) because of the formation of an oxide film at the interface. It may be a specific issue to assess the localisation of the cold point in a particular system and to compare it to the interface temperature, so as to avoid as far as possible the formation of a thick impurities layer on the interface. This purification by sedimentation is the choice made for the MEGAPIE experiment, prior to its filling operation; where oxides and impurities will be kept in storage vessels [Courouau, 2004c, 2005a], but still require validation.
The filtration system, possibly at the coldest point of the facility, appears as one of the most suitable processes for the lead alloy coolant. This operation is typically a chemical engineering operation, difficult and complex to investigate in liquid metal. Its efficiency depends on numerous parameters, constants or variables during the operations. The main factors of importance are as follows:

- location in the systems, geometry, etc.;
- driving force that induces the flow through the media, regeneration ability;
- operating parameters: flow rate, temperature, etc.;
- solid: nature, form and size, concentration, and particles size distribution;
- filter medium: nature, surface, thickness, pore size, hydrodynamic resistance, mechanical resistance, mode of operation (continuous or batch), pressure and temperature for the filtration, etc.

The particle size distribution defines the choice of the filtration medium. The liquid presenting a large amount of particles of small size (1 μm or less, colloidal) will clog quickly the filtration medium by the formation of little permeable, and compact deposit on the filtration medium (“cake”). The filtration rate will slow down drastically. Particle size distribution might be modified by some process such as coagulation to increase the filtration efficiency. If particles are roughly spherical, the cake will have a good permeability to the liquid, and thus a large filtration rate. Another illustration is available for the elastic or compressible particles, that will act as valves, as any increase of the driving force will decrease the filtration rate, due the compaction of the cake, and a sharp decrease of the pore size [Perry, 1997].

There are typically two types of filtration mechanisms that could be applied to liquid metal technology for separating a solid from a liquid [Perry, 1997]:

- deep bed filtration where solids are trapped within the pores or body of the filter medium;
- cake filtration where solids are stopped at the surface of a filter medium and pile upon one another to form a cake of increasing thickness.

From the lead alloys operating feedback, the following filtering media for deep bed filtration is reported: alumina fibre in the form of textile; glass fibre; metallic mesh textile like or sintered metal filter [Zrodnikov, 2003], [Orlov, 2005].

From the aluminium refinery technologies for advanced applications (aerospace), the use of filtering medium for deep bed filtration, such as alumina foam or zircon-mullite honeycomb medium is reported for the removal of tiny particles before the metal casting operation as once-through operation. In addition, a magnetic field is reported to have promoted the nucleation and crystal growth as well as adsorption on specific metal. There is then a variety of solutions, but, as the basic data are missing, nature of particles, size, form, etc., as well as the filtration rate, so that there neither current design rules or selection criteria are well defined, except for the pressed and sintered fibre metal medium developed for BREST-300 [Papovyants, 1998], [Orlov, 2005].

As the unit will eventually be plugged, it sounds logical either to design the system for the whole service lifetime, or to provide systems with an easy removal and replacement, or regeneration of the filtration medium.

Moreover, nuclear systems purification must be designed to cope with incidental contamination such as the loss of cover gas tightness, water or other ingress (grease, oil, mercury, etc.), as their
impact lays on the loss of operating time because of the need for long and costly purification campaign. In the latter case of contamination, the oil ingress is by far the incident that happened the most often, as in the Prototype Fast Reactor of Dounray (UK-PFR) 1991 (150-200 l). The Russian feedback reports the effect of such an event on lead alloy system (KV-27 land reactor), which is very similar to the sodium-oil pyrolysis reaction giving solid materials [Ivanov, 2003a].

4.3.3 Active impurities

The control of the radioactive impurities topic will not be fully addressed, as it is a complete realm of studies by itself (see Chapter 5), so that only some elements are given hereafter, and particularly supported by one fully documented case study [Petrovich, 2002], in order to sort out which of the active nuclides could be critical for a nuclear system operation, and to focus on some basic hard points for further studies, such as the behaviour of the volatile species (noble gas, Po, Hg, Cs, I), or the mobile species (tritium), or the long half-life nuclides that will affect the maintenance operations during shutdown, and later the waste management for decommissioning. Until now literature insisted mainly on the polonium nuclides production.

4.3.4 Production rates assessment

The activation/spallation sources are continuous and important in term of activities as well as in term of potential dose rate. However, this point should be more fully addressed in order to take provision to the fact that lead is often used as biological shielding to limit the dose rate.

To support the following analysis, figures that were assessed by [Petrovich, 2002] for a primary circuit of a subcritical system, which can be assumed as representative of critical system, as well as for the spallation target circuit, will be taken into account. These calculations correspond to the TECLA project reference subcritical reactor: 300 MWth, 3.7 tonnes of LBE for the target, 2000 tonnes for the LBE coolant loop, 3 mA for the nominal beam current, 0.6 to 1.5 GeV for the beam energy [Courouau, 2003a]. The codes used for the following assessment are MCNPX and SP-FISPACT [Petrovich, 2002].

The most abundant nuclides produced by the spallation reactions are the nuclides close in mass to the lead and bismuth, such as Po, Tl, Hg, and Au, directly descending from the spallation and activation reactions, which basically peel off neutrons from the nucleus. In fact, including all direct reactions and daughter reactions, almost all the periodic table is produced with a clear peak close to the atomic number of the lead or bismuth, and a second one at about half the value. There is about 3 to 4 orders of magnitude difference between the impurities concentrations observed in the target and in the coolant. As regards impurities production, the mass rates are low when compared to other potential source of impurities in the system such as the corrosion source, except for Po in the primary loop where the amount of Bi under the neutron flux is very large, and Po, Hg, Tl, Au, Os and Ir for the target loop:

- target loop: 180 g per operating year (163 g for Po, Hg, Tl, Au, Os and Ir);
- primary loop: 2970 g per operating year (2940 g of Po and 29 g of Tl, Hg, Au and Pt).

As regards the chemistry of these systems, one can only considerer at first the influence of these few impurities:

- target loop: Po, Hg, Tl, Au, Os and Ir;
- primary loop: Po and to a less extent Tl, Hg, Au.
However, possible phenomena occurring in these systems and leading to a local accumulation (plugging), or local effect (corrosion inhibitors or promoters) are to be ascertained, as well as the gas-liquid interactions (Po, Hg, Cs, etc.) and the effect on the control of the dissolved oxygen content.

After one year of irradiation at 3 mA, the total activity of the LBE of the target loop is assessed as being 44300 TBq for the 3.7 tonnes of LBE that makes 12 TBq/kg or 320 Ci/kg. This level of activity appears exceptionally high when considering fluid activity in typical nuclear power plant operation, although it is quite rational in the realm of the high neutrons source. The total activity of the primary loop is assessed as being 1.1 \(10^{18}\) Bq for the 2000 tonnes of LBE, which makes 0.55 TBq/kg or 15 Ci/kg almost only due to \(^{210}\)Bi (52%) and \(^{210}\)Po (43%). The elements giving the highest activities after the coolant and polonium nuclides are the following: Tl, Hg, Au, Pt, Ir, Os, and Re. While the activity of Tl is only about one order of magnitude lower when compared to the coolant, the Re activity is 5 orders of magnitude less. Except for the lead and bismuth isotopes, which represent the coolant activation itself and which are numerous as expected, most of the activity is due to the isotopes of Po, Tl, Hg, Au, Pt, and Ir, listed in decreasing activity order.

Then, after one year of radioactive decay, the total activity of the spallation target decreases by a factor of 35, but is still significant: 1260 TBq that makes 0.340 TBq/kg. Main contributions are the following: \(^{210}\)Po (75% of the total activity), \(^{195}\)Au (9.5%), \(^{207}\)Bi (4.5%), \(^{206}\)Tl (3.5%), \(^{185}\)Os (1.1%) and \(^{208}\)Po (1.5%). The main nuclides responsible for the dose rate are then: \(^{185}\)Os (3.6 \(10^6\) Bq/g), \(^{88}\)Y (2.55 \(10^5\) Bq/g), \(^{192}\)Ir (2.24 \(10^5\) Bq/g), \(^{99}\)Zr (6.9 \(10^4\) Bq/g), with the assumption of a linear relation between the dose rate and the activity.

For the coolant loop, the residual nuclides responsible of 99% of the total dose rate are listed as follows in decreasing order of dose rate contribution: \(^{207}\)Bi(\(\gamma\) \(+\), 37.97 y – 2 \(10^4\) Bq/g supposing a perfect homogeneity within coolant), \(^{210}\)Po (\(\alpha\), 138.4 d – 4 \(10^7\) Bq/g), \(^{185}\)Os (\(\gamma\) \(+\), 93.6 d – 73 Bq/g), \(^{208}\)Tl (\(\gamma\) \(+\), 3.67 y – 9 Bq/g), \(^{164}\)Pm (\(\gamma\) \(+\), 363.42 d – 16 Bq/g), and \(^{195}\)Au (\(\gamma\) \(+\), 186 d – 4500 Bq/g)

To the spallation residues, the activation products should be added for both the coolant and the target loops:

- activation of the coolant, lead and bismuth, which makes up, along with the spallation residues, the largest part of the total activity, as previously illustrated;
- activation of dissolved impurities by the neutron flux, intrinsic impurities from the supplied alloys such as Ag, corrosion products, etc.;
- release of activated products by the corrosion, dissolution of structures submitted to the neutrons.

Then, due to mass transfer and deposition, the activated corrosion products can plate out on different parts of the circuit, being for instance responsible of significant dose rates for the personnel during maintenance and handling operations of some specific component such as pumps, heat exchangers, etc.

To the spallation and activation products, fissions products are released into the primary coolant loop: tritium and fissile products.

Tritium is produced by fission and spallation. This nuclide is rather particular for a reactor system, as it is very mobile throughout hot and metallic interfaces immersed in liquid metal. Although tritium have a low energy activity (beta), it is accounted for as it migrates, is present in section of the reactor where no other radioactive product is expected and is finally released to the environment,
where, as HTO, can have a significant dose impact, if it is not mastered. This is why tritium was studied for the prediction of release rates or inventories in various subsystems, at the time of the design or during operation.

Fissile contamination sources in normal operation are due to surface contamination of the fuel cladding by traces of Pu or U. These traces migrate into the liquid metal, and account for fissile contamination of the coolant. In addition, when subjected to the neutron flux, fission products appear, such as caesium and iodine nuclides, but at very low level. In case of fuel-cladding failure, volatile fission products such as caesium, iodine, xenon and krypton nuclides are released in the system, mostly in the cover gas, in much larger quantities.

4.3.5 Consequences on operations

By contrast to the spallation target which present a small service lifetime with no maintenance nor repairing, the primary circuit is planned for the whole reactor service lifetime (tens of years), which necessarily requires maintenance operations, component handling, refuelling, etc., and might require the use of specific radioactivity control system.

The behaviour of these nuclides depends on their chemical form in the liquid lead alloys:

- dissolved, if the solubility is large when compared to the mass released (Au for instance);
- dissolved, but submitted to precipitation if solubility is low enough in some part of the circuit when compared to the mass released;
- oxidised, if the oxide potential is lower than lead oxide, and depending on oxygen potential of the liquid alloy.

As previously seen, some active nuclides may build-up in specific parts of the system, such as the cold exchange surfaces of heat exchangers, or at the gas-liquid interface, or on other specific spots. This will not have any impact on operations, but during maintenance and component handling, this may lead to the necessity to perform cleaning and decontamination operations.

As the dose rate of the primary coolant is mainly due to $^{207m}$Pb, with a level not comparable to any other nuclide, it is critical for designing the biological shielding. However, this nuclide disappears in less than one hour as its half-life is only of 0.8 s, so that other nuclides are to be considered for maintenance or handling operations, and even for the dismantling.

The coolant activation itself influences the operations related to components of fuel handling for maintenance, or repair, as they may require specific operations to allow repair, increasing the overall reactor complexity, as:

- coolant cleaning process to remove the coolant itself;
- decontamination process by acid attack to remove the deposits and first micrometers of the structure, and decrease the activity and dose rate due to nuclides adsorbed into the steel.

In addition, the nuclides, which can transfer from the liquid coolant to another system such as secondary or auxiliary system, cover gas control system, etc., are the main source of concern during normal operating mode, as they may require specific control and processes to keep them within the release authorisations specified by the safety authorities:
• tritium, as it makes up one of the main contributions to the release to the environment;
• volatile species such as Kr, Br, Xe, Ar, I, Cs, H, Po, and Hg nuclides.

Depending on the cover gas system, various solutions can be implemented to control the activities, such as for instance:

• Re-circulating cover gas loop, which can include some delay tanks to increase residence-time and favour radioactive decay of short half-life products (Kr), or trapping on charcoal bed (Xe), or even cryogenic trap, all of which were used for the liquid sodium fast reactor systems. Other specific traps for Po compound or mercury vapour could be designed to reduce coolant activity from those radioisotopes specific to lead alloys system.
• Gas tight system, with venting from time to time to relieve the pressure, with the necessary gas decontamination before release to the stack, as foreseen for the MEGAPIE target operation.

It may be a solution for the polonium nuclides to use their volatility properties (PoPb compound) to eliminate it in the gas phase rather than in the liquid phase, as it could be easier. The effect of the oxygen control process that requires gas flowing to either oxidise or reduce the lead alloys is to be addressed from this activity control issue, as it will affect the gas-liquid distribution of the active nuclides as well. This is especially true for the hydrogen/steam gaseous mixture bubbling or cover gas blowing, as:

• H$_2$Po, is volatile, so that the process will enhance the Po transfer to the gas phase.
• Tritium, as a hydrogen isotope, will react isotopically with H$_2$ from the gas phase as well as with the steam, so that the reaction will favour the tritium transfer to the gas phase.

During incidental events, such as the loss of coolant accident, the alpha emitters activity in the lead alloy is often the dimensioning event for the safety scenario. In that case, this allows setting up the specification of the maximum $^{210}$Po nuclide that could be agreed in the coolant loop, so as to study and design the necessary control processes [Khorosanov, 2002], [Buongiorno, 2004].

4.4 Instrumentations for chemical monitoring

4.4.1 On-line electrochemical oxygen sensor

The accurate measurement of the oxygen concentration in the liquid lead-bismuth eutectic, as well as in the pure lead alloys for use as coolant in nuclear systems or as liquid spallation target for high neutrons source or accelerator-driven system is a critical issue for defining the active oxygen control that will first of all prevent the contamination of the liquid system by lead and bismuth oxides, as well as, possibly, to ensure an efficient corrosion protection of the iron based alloys structures if the self-healing oxide layer method is chosen.

The use of the ionic conduction properties of some solid electrolyte [Desportes, 1994], and in particular the zirconia based ceramic, allow to make electrochemical cell assembly that allows the measurement of dissolved oxygen in liquid metal system, whose activity could be extremely low ($<10^{-4}$). This is known as the electromotive force measurement in open circuit or as the galvanic cell method.
This technique presents several well-known advantages such as:

- specific to the dissolved oxygen, but the bounded oxygen, such as in oxide, is not taken into account;
- rapid and continuous measurement, that is able to be implemented directly on-line in the system, provided the leak tightness of the seal in between the liquid metal and the ceramic;
- wide concentration range covered by one single sensor, with a lower detection limit that is actually very low, as well as its potential operating temperature range;
- no relation with the size and contact area of the electrodes;
- no disturbance on the measured system.

However, its well-known limitation was its use at a rather high operating temperature, in the order of 750°C typically for a Pt-air reference system, because of the high cell resistance that increases with decreasing temperature, as well as the irreversibility of the cell. In addition, the poor thermal shock resistance requires special care to prevent high thermally induced stresses that can cause cracking of the solid electrolyte. A specific protection from rapid temperature fluctuation shall be provided.

Another solution is to design sensor as a consumable item. The service life is often reported as being in the range of the tens to hundreds of hours only.

Although the principle and the application have been well known since the 50s, especially at the laboratory scale for the measurement of basics thermodynamic data, its real application as industrial oxygen sensors began in the late 80s where its applications covered lots of applications, from the automotive industries (lambda sensors) to glove box gas control [Desportes, 1994]. However, some particular and earlier applications such as the sensor for the steel making industry, which is used to measure C/CO ratio, as well as the sensor for the liquid sodium to be used as nuclear coolant (yttria-stabilised thoria), could be noticed [Asher, 1988]. In addition, the Russian institutes developed a specific application for the oxygen control in lead-bismuth eutectic to be used as coolant in nuclear submarines in the late 70s-80s [Gromov, 1997, 1998], [Shmatko, 2000], whose teams paved the ways for this very specific instrumentation in heavy liquid metal coolant with the use of very specific multi layers pellet type sensor [Shmatko, 2000]. This specific design of the solid electrolyte, although very complicated and costly to produce (pellet type, multilayer ceramics, metal to ceramic bonding...), allowed a very accurate measurement of the oxygen together with an exceptionally long service lifetime of 10 years. Some of these sensors are still in use in Russia, as well as in Italy [Azzati, 2003], but are apparently no longer produced. Since the mid-90s, development and testing of new sensor design based on yttria-stabilised zirconia or magnesia-stabilised zirconia were conducted worldwide, including in Russia [Askhadulline, 2003, 2005], [Chernov, 2003], [Colominas, 2004], [Courouau, 2002b, 2004a], [Fernandez, 2002], [Ghetta, 2002], [Konys, 2001, 2004], [Li, 2003], [Muscher, 2001], [Zrodnikov, 2003], [Takahashi, 2002].

The main requirements for an on-line oxygen sensor are as follows: accurate in such a low oxygen concentration range, reliable, predictable and safe for long-term nuclear operation. For instance, one of the main constraints as regards the safety for such system is related to the ceramic breakdown: any leaks of radioactive liquid metal outside the system must be prevented, as well as any ceramic pieces running in the nuclear loop. However, some limitations appeared on some sensors using the commercially available yttria-doped zirconia thimble [Courouau, 2005b], such as the ceramic relative fragility, as well as the time drift that is often observed that will delay for a while their direct implementation on nuclear system. However, the new Russian sensor design [Zrodnikov, 2003] was already used in the nuclear loop of the BOR-60 lead channel [Korotkov, 2003], which operated for
about 100 days. For this sensor, not only the shape (conical when compared to one-end closed tube) but also the composition of the solid electrolyte is adjusted to enhance the ceramic resistance to thermally induced stresses [Askhadulline, 2005].

4.4.1.1 Principle

Sensors are based on the potential measurement method at null current for a galvanic cell built with a solid electrolyte: zirconia doped with either magnesia, calcia or yttria, as this doping element stabilises the ceramic into the tetragonal form that is oxygen ions conducting for a certain temperature and oxygen conditions. Although the Russian feedback indicated the achievement of such sensors for the low operating conditions expected of the lead alloys [Gromov, 1997], [Shmatko, 2000], their assembly was not straightforward at first as it was considered that such electrodes and cells would not work for the temperature of interest for the lead alloys applications (400 to 550°C), because of the irreversibility of the electrode, and because of the too high cell resistance.

The electrodes define either the liquid metal phase where the dissolved oxygen is to be measured, the working electrode, as well as the reference electrode, which is the constant oxygen potential reference system, as illustrated in Figure 4.4.1.

Figure 4.4.1. Galvanic cell principle

![Galvanic cell principle](image)

Sensors assembly is made within the laboratory and is now considered as a routine procedure, as illustrated in Figure 4.4.2, where the use of the one-end closed tube allow separating easily the reference (inside) from the measurement medium (outside). One of the critical elements for the design of such sensor is then the sealing between the ceramic tube and the structure of the liquid metal system, which must be leak tight as well as electrically insulated.

Figure 4.4.2. Generic implementation scheme from [Konys, 2001]
The solid electrolyte supplied by FRIATEC AG company (yttria-doped zirconia, FzY grade, 8.1% in yttria) was used by [Courouau, 2003b] and [Konys, 2001] for instance whereas FERROTROM company supplied the ceramic used by IQS (both magnesia- and yttria-stabilised zirconia) [Colominas, 2004], while some other suppliers can be found worldwide [Li, 2003], or Nikkato Corporation [Ganesan, 2006]. On-purpose ceramic can be synthesised and fired with the required characteristics and shape [Shmatko, 2000], [Ashhadulline, 2005]. This supplier list is not exhaustive.

Assembly is done in the open air. Ingots of pure metal and oxides powder are mixed to get a liquid metal internal reference at the operating temperature with only a slight excess of its oxide; 10% to 50% of oxides in excess are reported as satisfactory [Courouau, 2003a]. The air in excess is consumed during the first use, corresponding to the activation of the sensor, to form oxide of the reference metal. The activation of the sensor is done during the calibration procedure or during its first use, the first step of which is the immersion of the sensor in a LBE melt followed by a temperature increase. Once the sensor is giving a stable potential output (electromotive force – emf), the reference is considered at the thermodynamic equilibrium, and the sensor is said activated or ready for operation. This is done in a matter of minutes at 450-500°C.

The choice of the reference system is critical. It depends widely on various parameters [Desportes, 1994], such as the oxygen partial pressure of the reference, which must be close to the partial pressure to be measured, the good knowledge of the equilibrium value of the reference system, a good buffering effect in case of slight disturbances to keep the partial pressure stable, and good compatibility between the lead wire and the reference systems. The use of gas (air, or oxygen) present some advantages, as the partial pressure is accurately known, whereas the thermodynamic data of the liquid metal reference couple metal/metal oxide could be less accurately known, requiring a calibration [Desportes, 1994].

Usually air is used with platinum coated on the ceramic surface for a better junction at the interface, and a Pt lead wire, making the Pt/air electrode, with a well-known limitation in its operating temperature, because of the resistance of the junction between the gas and the solid phase. The operating temperature must be higher than 450°C for such a cell [Desportes, 1994], [Konys, 2004]. To the opposite, liquid metal reference systems provide a better contact with the solid electrolyte, and then a lower cell resistance at comparatively lower temperature. The use of low melting point metal allows favouring the use of the sensor in the required temperature range of a lead alloy system (400-500°C), without an additional heating system.

The effect of thermal cycling on the solid electrolyte when a liquid metal reference is used can be critical. Indeed, the melting /cooling of the internal reference can induce wears on the solid electrolyte, promoting the growth of microcracks, eventually leading to the rupture [Courouau, 2005], whereas the air/Pt electrode used in the same conditions of liquid metal electrode exhibited a much higher service lifetime [Konys, 2004].

The contact lead wire must be compatible with the liquid metal melt of the reference. For instance, molybdenum presents a low solubility in bismuth, which is favourable. To the opposite, platinum or iridium metal, which are the typical lead wired for such electrochemical cell, dissolve in liquid bismuth, forbidding their use on the long term.

The reference electrode must not chemically react with the solid electrolyte, leading to the formation of reaction products on the interface, modifying the potential outputs. Similarly, it must not represent a source of contamination in case of ceramic failure. Bismuth is chemically close to lead, fully miscible, and its oxide is less stable than lead oxide. On the other hand, indium that was used extensively for the Harwell oxygen meter, forms more stable oxide than lead, so that it will reduce the oxygen potential of the liquid lead alloys.
The range of the readings for the indium reference electrode latter system presents a null voltage output, which does not mean that the sensor is broken. This clearly represents an operating difficulty, as in that case, there is no straight possibility to conclude between the effectiveness or the failure of the sensor. An example of that behaviour was observed during STELLA operation (Figure 4.4.5), where the In sensor was believed broken for several days, and several time when its output was close to the null value. This point discards, a priori, this reference system for nuclear operation, unless systematic and standard calibration could be developed for a periodic checking of the sensor.

These considerations explain why the choice for the reference systems focused mainly on either the gas system (air-Pt lead wire) or the bismuth (mp. 271°C)/bismuth oxide or indium (mp. 157°C)/indium oxide systems for the reference electrode with Mo as lead wire, although other reference could be used in principle. From the safety point of view, the gas reference system will not be favoured for use in a nuclear system, as it requires the constant flowing of gas inside in the reference electrode, making the route for the contamination of activated lead alloys outside the confinement in case of failure of the solid electrolyte.

4.4.1.2 Theory

This analysis is done for pure lead as well as for the lead-bismuth (55% in weight) eutectic.

The method of the potential measurement with null current can be applied to the measurement of the dissolved oxygen in liquid lead-bismuth alloys. A typical electrochemical galvanic cell that will be subsequently referred to as “EC sensor” is as follows:

Mo, Metal + metal oxide (reference) // ZrO2 + Y2O3 // Pb + PbO (lead alloy solution), steel

where the yttria-stabilised zirconia (YSZ) ceramic, which conducts specifically oxygen ions, separates two medias showing different oxygen activities; an electromotive force (emf) is then formed across the solid electrolyte. If one of the media is defined to act as a reference, so as to maintain constant the oxygen partial pressure to a defined value, then the emf is a function of the oxygen activity in the other medium.

Assuming pure ionic conduction in the solid electrolyte, and assuming that all transfers at the various interfaces developed in the electrochemical cell are reversible, the Nernst relation giving the theoretical emf, noted \( E_{th} \), can be written:

\[
E_{th} = \frac{RT}{4F} \ln \frac{P_{O_{2}(reference)}}{P_{O_{2}}} \quad (4.20)
\]

with \( E_{th} \) in Volts, \( R \) the perfect gas constant (8.31441 J/mol/K), \( F \) the Faraday constant (96484.6 C/mol), \( T \) the temperature (Kelvin), and \( P_{O_{2}} \) the oxygen partial pressure in the lead alloy.

The oxygen partial pressure of the reference, \( P_{O_{2}(reference)} \), is defined by the following reaction, in case of a metal (M)/metal oxide (M\(_x\)O\(_y\)) reference, where \( x \) and \( y \) are respectively the stoichiometric coefficients for the metal and the oxygen.

\[
\frac{2x}{y} M_{(liquid)} + O_2 \Leftrightarrow \frac{2}{y} M_{(solid)} O_{(solid)} \quad (4.21)
\]
All reactions are written so that it corresponds to the consumption of one mole of oxygen. The units of the free enthalpies of formation are then expressed in J/mol of oxygen O₂.

As the reference is built so as to present a constant oxygen partial pressure, both the metal and its oxide are present in excess to ensure the thermodynamic equilibrium of the reaction. In addition, the liquid solution corresponds to the pure metal, so that the activities of both the reference and its oxide are equal to one and then:

\[ \ln P_{O_2 \text{ reference}} = \frac{\Delta_f G^0_{\text{reference}}}{RT} \]  

The oxygen partial pressure in the lead alloy melt, is given by the thermodynamic equilibrium of lead monoxide, considering that it is the most stable oxide in lead bismuth eutectic.

\[ 2Pb_{(\text{liquid})} + O_{2(gas)} \rightleftharpoons 2PbO_{(\text{dissolved})} \]  

The activities product of the lead oxide reaction of formation in lead alloys is then as follows using the oxygen activity defined in Eq. (4.3),

\[ \Delta_f G^0_{PbO} = -RT \cdot \ln \frac{a_{PbO}^2}{a_{Pb}^2 \cdot P_{O_2}} \text{ and then } \ln P_{O_2} = \frac{\Delta_f G^0_{PbO}}{RT} + 2 \cdot \ln \frac{a_O}{a_{Pb}} \]  

The saturated oxygen concentration for lead and LBE are derived from Eq. (4.1) and Eq. (4.2):

\[ \text{Lead: } \ln C_{O(wgr\%)} = A - \frac{B}{T_{(K)}} \text{ with } A = 7.3683 \text{ and } B = 11512.925 \]  
\[ \text{LBE: } \ln C_{O(wgr\%)} = A' - \frac{B'}{T_{(K)}} \text{ with } A' = 2.7631 \text{ and } B' = 7828.789 \]  

Lead activity is equal to unity in pure lead solution, and is given by the following Russian relation in LBE solution as quoted in [Courouau, 2002b]:

\[ \text{LBE: } \ln a_{Pb} = -\alpha - \frac{\beta}{T_{(K)}} \text{ with } \alpha = 0.8598 \text{ and } \beta = 135.21 \]  

The free enthalpies of formation for the various oxides are expressed by the following relations, assuming that all relations are given for the consumption of one mole of O₂:

\[ \Delta G^0_{(J/mol)} = \Delta H^o - \Delta S^o \cdot T_{(K)} \]  

Calculations are made with the help of the HSC database software [HSC, v4.1], which represents a compilation of some of the latest thermodynamic data available. The free energies of formation are linearly regressed on a limited temperature range, 400-1000 K, so as to determine the standards enthalpy and entropy by the least mean squares method. The latter data, standard enthalpy and entropy, are constant over the temperature range (cf. Table 4.4.1)
Table 4.4.1. Main oxides free enthalpies coefficients for the 400-1000 Kelvin temperature range per mole of oxygen $O_2$ consumed

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^o$</th>
<th>$\Delta H^o$</th>
<th>$\Delta S^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(400-1000 K)</td>
<td>J/mol</td>
<td>(400-1000 K)</td>
</tr>
<tr>
<td>$\frac{4}{3}$ Bi + $O_2$ = $\frac{2}{3}$ Bi$_2$O$_3$</td>
<td>-389140</td>
<td>-192.6</td>
<td></td>
</tr>
<tr>
<td>$2$ Pb + $O_2$ = $2$ PbO</td>
<td>-437608</td>
<td>-199.1</td>
<td></td>
</tr>
<tr>
<td>$\frac{4}{3}$ In + $O_2$ = $\frac{2}{3}$ In$_2$O$_3$</td>
<td>-618674</td>
<td>-216.8</td>
<td></td>
</tr>
</tbody>
</table>

The general relationship for a metal-metal oxide reference could then be derived from the Nernst relation, assuming a pure ionic conduction in the solid electrolyte:

$$E_{th} = \frac{\Delta G^o_{\text{reference}} - \Delta G^o_{\text{PbO}}}{4F} - \frac{RT}{2F} \ln \frac{a_o}{a_{\text{Pb}}},$$

(4.29)

By using the following constants:

$$a = \frac{\Delta H^o_{\text{reference}} - \Delta H^o_{\text{PbO}}}{4F},$$

(4.30)

$$b = -\frac{\left(\Delta S^o_{\text{reference}} - \Delta S^o_{\text{PbO}}\right)}{4F},$$

(4.31)

$$c = -\frac{R}{2F}.$$  

(4.32)

These constants allow to writing down simplified relations:

**Lead:**

$$E_{th(V)} = a + b \cdot T_{(K)} + c \cdot T_{(K)} \cdot \ln a_o,$$

(4.33)

**LBE:**

$$E_{th(V)} = (a + c\beta) + (b + c\alpha) \cdot T_{(K)} + c \cdot T_{(K)} \cdot \ln a_o,$$

(4.34)

Hence for saturated oxygen solution, the previous relations depend only on the temperature:

**Lead:**

$$E^{\text{SAT}}_{th(V)} = a + b \cdot T_{(K)}$$

(4.35)

**LBE:**

$$E^{\text{SAT}}_{th(V)} = (a + c\beta) + (b + c\alpha) \cdot T_{(K)}$$

(4.36)

Finally, these general relations could be simplified by using the (a,b,c) constants and the concentration expressed in wt. %:

**Lead:**

$$E_{th(V)} = \left(a + cB\right) + \left(b - cA\right) \cdot T_{(K)} + c \cdot T_{(K)} \cdot \ln C_{O(\text{wt.%})},$$

(4.37)

**LBE:**

$$E_{th(V)} = \left(a + c\beta + cB\right) + \left(b + c\alpha - cA\right) \cdot T_{(K)} + c \cdot T_{(K)} \cdot \ln C_{O(\text{wt.%})},$$

(4.38)
The free energies are in good agreement with the respective energies computed with the use of other databases [JANAF], [Barin, 1989]. The slight inaccuracy of these data will affect the theoretical electromotive force calculation by a few millivolts that are assumed as reasonable. Another source of scattering is due to the data coming from the lead activity relation in LBE, which affect only slightly the emf by a maximum of 10 mV, as well as from the oxygen solubility relation, which can affects, on the contrary, the emf to a much greater extent. This is why it is essential to know with a relatively high accuracy the oxygen solubility data (cf. Chapter 3). All calculations presented here are made with Eq. (4.1) and Eq. (4.2) respectively for lead and LBE.

The constants of the Nernst relations can then be calculated, and are reported in the next table for Bi/Bi2O3 and In/In2O3 reference electrodes for a cell immersed into a lead alloy melt according to the following emf \( E \) vs. temperature \( T \) and oxygen concentration \( C_o \) relationships:

\[
E_{(mV)} = K_1 + K_2 \cdot T(K) + K_3 \cdot T(K) \cdot \ln C_o \text{ (ppm weight)}\quad \text{for } E > E_{sat} (4.39)
\]

\[
E^{SAT}_{(mV)} = K + K' \cdot T(K)\quad \text{for } E = E_{sat} (4.40)
\]

These relations enables to plot the \( E \) vs. \( T \) (\( C_o \) as parameter) diagram as illustrated in Figure 4.4.3, which are most useful for reading sensor output as well as for calibration of sensor [Konys, 2001], [Gromov, 1998]. It allows plotting the reading easily and to compare the relative position of the oxygen when compared to the PbO saturation line, defining the lower potential value achievable, which must be avoided to keep clear from the contamination by PbO precipitation. Similarly, other oxide stability threshold can be plotted for a direct information on the position of the oxygen potential when compared for instance to the stability of the magnetite.

**Figure 4.4.3. Diagram \( E \) vs. \( T \) for the oxygen sensor reading in LBE**

Indicates the oxygen iso-concentration lines, as well as the PbO saturation and the Fe3O4 stability lines for an iron activity of one, the iron oxide being stable below the line. For a lower iron activity, meaning a concentration lower than its solubility, the potential threshold for the dissolution of the magnetite will be lower.

Apart from the data used for the theoretical assessment, there may be other causes for the sensor not to behave according to the theoretical relations: electrolyte conduction properties (slight electronic conduction, impurities in the ceramic, etc.), the influence of the reaction at the electrode/electrolyte
interface (liquid metal/zirconia reaction, or even traces of impurities depositing on the interface), the cell irreversibility (equilibrium not reached due to an oxygen transfer rate limitation especially at very low oxygen partial pressure), as well as the instrumental uncertainties. This is why calibration methods are often required [Subbarao, 1980], [Courouau, 2003b].

Table 4.4.2 synthesises the most useful relations for In and Bi reference sensor in LBE melts.

### Table 4.4.2. Theoretical relations for Bi/Bi₂O₃ and In/In₂O₃ references for LBE melts

<table>
<thead>
<tr>
<th>LBE</th>
<th>Bi/Bi₂O₃ reference (melting point 271°C)</th>
<th>In/In₂O₃ reference (melting point 157°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eₘₐₓ(T)</td>
<td>( E_{\text{SAT}}(\text{mV}) = 119.8 - 0.0539 \cdot T )</td>
<td>( E_{\text{SAT}}(\text{mV}) = -475 + 0.0088 \cdot T )</td>
</tr>
<tr>
<td>E(T, aₒ), E &gt; Eₘₐₓ(T)</td>
<td>( E(\text{mV}) = 119.8 - 0.0539 \cdot T - 0.0431 \cdot T \cdot \ln aₒ )</td>
<td>( E(\text{mV}) = -475 + 0.0088 \cdot T - 0.0431 \cdot T \cdot \ln aₒ )</td>
</tr>
<tr>
<td>E(T, Cₒ), E &gt; Eₘₐₓ(T)</td>
<td>( E(\text{mV}) = -218 + 0.0652 \cdot T - 0.0431 \cdot T \cdot \ln Cₒ(\text{ppm}) )</td>
<td>( E(\text{mV}) = -812 + 0.1279 \cdot T - 0.0431 \cdot T \cdot \ln Cₒ(\text{ppm}) )</td>
</tr>
<tr>
<td>( \ln aₒ(\text{T}, E) ), E &gt; Eₘₐₓ(T)</td>
<td>( \ln aₒ = -23209 \cdot \frac{E(\text{mV})}{T} + 2780 \frac{T}{T} - 1.251 )</td>
<td>( \ln aₒ = -23.209 \cdot \frac{E(\text{mV})}{T} - 11024 \frac{T}{T} + 0.205 )</td>
</tr>
<tr>
<td>( \ln Cₒ(\text{T}, E) ), E &gt; Eₘₐₓ(T)</td>
<td>( \ln Cₒ(\text{ppm}) = -23.21 \cdot \frac{E(\text{mV})}{T} - 5049 \frac{T}{T} + 10.723 )</td>
<td>( \ln Cₒ(\text{ppm}) = -23.21 \cdot \frac{E(\text{mV})}{T} - 18853 \frac{T}{T} + 12.178 )</td>
</tr>
<tr>
<td>( \ln P_{\text{SAT} \ O₂} ), E = Eₘₐₓ(T)</td>
<td>( \ln P_{\text{SAT} \ O₂} = -52362 \frac{T}{T} + 25.67 )</td>
<td></td>
</tr>
<tr>
<td>( \ln P_{\text{O₂}} ), E = Eₘₐₓ(T)</td>
<td>( \ln P_{\text{O₂}} = -46803 \frac{T}{T} - 46.418 \frac{E}{T} + 23.16 )</td>
<td>( \ln P_{\text{O₂}} = -74413 \frac{T}{T} - 46.418 \frac{E}{T} + 26.075 )</td>
</tr>
</tbody>
</table>

Using another kind of reference sensor, the air/platinum reference sensor, described as follows, similar relations could be derived:

Pt, O₂ (reference) // ZrO₂ + Y₂O₃ // Pb + PbO (lead alloys solution), steel

\[ \text{Lead: } E_{\text{th}}(\text{V}) = \left( \frac{-\Delta H_{\text{PbO}}}{4F} + \frac{\Delta S_{\text{PbO}}}{4F} - \frac{c}{2} \ln 0.21 \right) \cdot T(K) \]  

\[ \text{Lead: } E_{\text{th}}(\text{V}) = \left( \frac{-\Delta H_{\text{PbO}}}{4F} + cB \right) + \left( \frac{\Delta S_{\text{PbO}}}{4F} - \frac{c}{2} \ln 0.21 - cA \right) \cdot T(K) \]  

\[ + c \cdot T(K) \cdot \ln C_{o(\text{ppm})} \]  

159
Finaly, these relations are calculated for the saturation using the data previously given using the oxygen concentration expressed in ppm (10⁻⁶ g/g):

\[
\text{Lead: } E_{\text{sat}}^{\text{mv}} = 1133.9 - 0.550 \cdot T_{(K)}
\]

\[
\text{Lead: } E_{\text{mv}} = 637.8 + 0.165 \cdot T_{(K)} - 0.043 \cdot T_{(K)} \cdot \ln C_{o(ppm)} \text{ for } E > E_{\text{sat}}
\]

\[
\text{LBE: } E_{\text{sat}}^{\text{mv}} = 1128.1 - 0.587 \cdot T_{(K)}
\]

\[
\text{LBE: } E_{\text{mv}} = 790.7 - 0.071 \cdot T_{(K)} - 0.043 \cdot T_{(K)} \cdot \ln C_{o(ppm)} \text{ for } E > E_{\text{sat}}
\]
However, a slight scatter of a few millivolts, up to several tens of millivolts is always observed from this theoretical behaviour that is not fully understood yet. The effect of the other impurities might be the source of the errors, by reacting at the solid electrolyte interface and forming metal/metal oxide couple interfering with the electrode potential. This would have to be understood more clearly as this side effect on the calibration process may limit the reliability of the sensors. The second source of errors is interpreted as coming from the zirconia intrinsic properties: slight impurity content variations in the fabrication process may be part of the explanation [Subbarao, 1980].

The temperature variation close to the oxygen saturation calibration method was repeated a large number of times so that mean statistical constants could be derived from it, and are then recommended instead of the use of the theoretical constants [Courouau, 2003b]:

\[
\begin{align*}
\frac{Bi}{Bi\text{O}_3} & \left\{ 
E^{SAT}_{(mV)} = 137 - 0.067 \cdot T_{(K)} \\
E_{(mV)} = -323 + 0.23 \cdot T - 0.0431 \cdot T \cdot \ln C_{o\text{(ppm)}}
\right. \\
\frac{In}{In\text{O}_3} & \left\{ 
E^{SAT}_{(mV)} = -412 - 0.051 \cdot T_{(K)} \\
E_{(mV)} = -937 + 0.71 \cdot T - 0.0431 \cdot T \cdot \ln C_{o\text{(ppm)}}
\right.
\end{align*}
\]

(4.50) (4.51)

The accuracy is assessed within 5% of the voltage readings (25 mV maximum scattering for a 500 mV reading) that affect the concentration by 40% for the high concentration range to 80% for the low concentration range. Calibration is, in any case, recommended to achieve a better accuracy. However, the availability of a method to achieve a reliable calibration on the field is necessary to significantly increase the accuracy on the long term, as well as to regularly assess the good operation of the sensor.

This is particularly critical as the time drift that was observed on several occasions on static device was recently confirmed by the STELLA loop operation (Figure 4.4.5). The drift appears only after a certain delay of several hundredths of hours, when the lead alloys was submitted to thermal and oxygen variations. Then, the drift gradually and almost constantly increases. In this specific example,
the Bi reference sensor exhibits the highest time drift, while the In reference sensor seems to keep a more consistent reading. The time drift of the Bi sensor is illustrated by plotting on the graph the absolute difference between the theoretical deviation between two different reference electrodes (546 mV here), and the difference between the two sensors readings:

\[ e = 546 - (E(Bi/ Bi_2O_3) - E(In/ In_2O_3)) \]

The value of \( e \) should be null according to theory, but, in practice, it is always equals to a few tens of mV, except when one of the sensors begins to significantly deviate from its normal behaviour.

Several hypotheses could be proposed to explain this deviation with time [Courouau, 2005b]: alteration of the interface of the electrode (working or reference) by oxide deposition, reaction with the LBE or the liquid metal reference, or alteration on the long term of the solid electrolyte interface by reaction with liquid metals, gases or even oxides. Basic investigation on broken sensor gave no clear results up to now as regards the Molybdenum lead wire, which could thermodynamically be oxidised by the liquid bismuth of the reference electrode, as the relative stability of the potential oxide is as follows: In_2O_3 > MoO_2, MoO_3 > Bi_2O_3 [Li, 2004].

The time drift understanding as well as the development of on-the-fields calibration method will enhance the overall sensor reliability, which are the basis of the ongoing research.

4.4.1.4 Characteristics of the oxygen sensors

Sensors have been tested for thousands of hours in both static and dynamic conditions in stable and unstable chemical conditions that validate their effective and reliable use for dynamic loop operation [Askhadulline, 2005], [Ghetta, 2002], [Colominas, 2004], [Courouau, 2003b], [Gromov, 1997], [Köyns, 2004], [Shmatko, 2000]. These tests allowed gaining a large operating feedback representative of long-term operations on a wide variety of operating conditions. The characteristics observed up to now on these oxygen prototypes sensors are then satisfactorily and confirm the previous observations, as regards the operating range (370°C-550°C for the Bi/Bi_2O_3 reference electrode), the oxygen concentration range, the response time, the accuracy and reproducibility, as well as the service life (several thousands of hours, longer expected in stable conditions). A lower operating temperature than 350°C is possible but with a lower accuracy as the sensor outputs deviate from ideal behaviour most probably because of an increasing irreversibility of the cell.
The time to react to a concentration change is fast for an oxygen contamination. The recovery time is linked to the chemical reaction kinetics that is limited by the mass transfer phenomenon (gas-liquid interface, oxygen diffusion in liquid bulk...). From a general point of view, the transient phase of one system is not absolutely reliable as the oxygen content is globally inhomogeneous. However, this effect disappears in steady state conditions. The sensor gives only the local oxygen content, so that the loop implementation is important to get reliable information of a homogenous system [Orlov, 2005].

The time drift is negligible with low oxygen concentration (<10⁻⁶ ppm) and stable operating conditions. Higher oxygen content (>10⁻⁶ ppm), or oxygen cycling, seems to affect the sensor output, reducing its service life. The other impurities present in the liquid metal may play a role as well. Another explanation is related to the electrolyte limitation itself. This could be solved by a cleaning operation (high temperature in low oxygen content, or, to be tested, a nitric acid washing of the zirconia). This is a point to be further studied, as this would possibly require a calibration procedure suited for loop operation, an on-the-field procedure, that is not available yet, as well as, if possible, a specific and complex regeneration procedure.

Although yttria-doped zirconia is known to present a better thermal shock resistance (temperature gradient, temperature cycling) as well as a better mechanical resistance when hot (vibrations, contact, etc.) when compared to other solid electrolytes such as yttria-stabilised thoria, a number of failures has been observed (Figure 4.4.6). The point of breakdown is often observed at the central point localised at the bottom of the ceramic thimble. The internal reference electrode when localised in a closed-end tube is itself a source of major mechanical wear during its solidification. Optic observations of the ruptured ceramic surface (Figure 4.4.6) indicate the gradual insertion of bismuth into microcracks most probably due to the positive volumetric change of Bi during its solidification. Lowering the height of the internal reference electrode will reduce this effect. The use of conical shape for the solid electrolyte is most favourable from this particular point of view, as the solidification constraints will exert preferentially upwards towards the free level rather than radially towards the ceramic. This conclusion is further evidenced by the experimental observations from the CORRIDA loop [Konys, 2004]: the air/Pt reference sensor exhibited a much higher service lifetime when compared to the Bi/Bi₂O₃ reference sensor used within the same operating conditions, and with the same electrolyte.

![Figure 4.4.6. Bi/Bi₂O₃ sensor operated for 1400 hours on the STELLA loop and details of the point of rupture [Courouau, 2005b]](image)

Another method to increase to reduce failures is to use a proper design for the ceramic housing, together with the use of special procedure for operation. This was typically used for the liquid sodium sensor (Westinghouse, Harwell) and is known as efficient [Asher, 1998]. Figure 4.4.7 presents one of the design for such a housing that has been achieved [Courouau, 2005b], and that must be validated on the STELLA loop. A similar design is used at the Karlsruhe Lead Laboratory [Konys, 2001]. Its main characteristics consist in having the seal ensuring the tightness of the facility between the ceramic and the metallic structure localised in the cold area, which is made possible thanks to the ceramic length,
This kind of design proved efficient in liquid sodium technology, as the sensor service lifetime was not depending from the sealing medium, which, if localised in the bottom area, would be in contact with high temperature liquid metal, eventually leading to a short circuit, or the loss of the leak proofness.

Although the closed-end tube shape is commercially available and easily separates the two electrodes, the working and the reference electrodes, it might have to be replaced by other less fragile shapes, like a conical shape sealed with graphite or tantalum [Li, 2003] or fused with a metal to ceramic bound [Chernov, 2003] to a metallic tube that is reported as far more resistant. However, the implementation becomes more complex because of the issue of the metal-to-ceramic sealing and fusing, without speaking of the cost of the specific fabrication of ceramic pieces. The Russian model, dating from the early 90s, and which is now registered in the Russian state standard committee (Figure 4.4.8), was, for instance, implemented on the BOR-60 lead channel and operated most satisfactorily during the irradiation time [Korotkov, 2003]. Recent developments include the inclusion of impurities, such as particles of alumina (nano size), as well as the specific firing procedure to exceptionally improve the mechanical resistance of the solid electrolyte [Askhadulline, 2005]. The more recent US model (Figure 4.4.9) is based on the solid electrolyte used in the car industry for the lambda sensor, whose ceramic part is then quite widely available at low cost. It is awaiting long-term validation in representative conditions for the long-term behaviour of the seal. In additions, a reactive braze for the bound was recently developed within the framework of a specific MIT-Ceramtec agreement with promising results up to now [Ballinger, 2006].

4.4.1.5 Conclusions

The oxygen monitoring system is quite compulsory for any lead alloy systems at least to ensure the contamination control. It is now clear that sensors based on solid electrolyte electrochemical cell proved efficient for measuring the dissolved oxygen of the lead alloys systems, despite a number of
limitations, which are quite typical of this kind of measurement. However, it is not commercially available, so that for a day-to-day use on experimental facilities, the theoretical background and know-how given in this section will allow the assembly of sensor from available part, as well as its basic use and allow interpreting its outputs.

Several concepts were designed and are presently at different level of achievement, but all are under rapid progress for a reliable use in a nuclear system. One can notice in particular the outstanding level of achievement of the Russian design, which presents, apparently, none of the limitations identified and described in this section, and was successfully used in a nuclear environment.

4.4.2 Development of sampling systems and analytical methods

The impurities monitoring system for the liquid phase is typical of the liquid metal fast reactors: a system that allows getting a liquid metal sample, in order to perform a chemical or radiochemical analysis of the impurities. A periodic sampling enables in principle to monitor the behaviour of the dissolved impurities on the long term as well as to assess the gradual activation of the coolant.

4.4.2.1 Dip sampler validation

There are two main different types of sampling system:

- dip sampling throughout an airlock system, which is the reference sampling system in liquid metal reactors such as the sodium-cooled;
- circulation in a tube-sampling device in a bypass line, which was partly given up because of representativeness difficulties as regards the corrosion products (potential accumulation due to deposits on the walls), although this is questionable depending of the impurities to be measured.
The objective is to be able to take a sample of liquid LBE in any facility to perform subsequent chemical analysis of the impurities. The following specifications are usually required for any sampling system:

- to obtain an homogeneous liquid metal sample;
- to provide a sampling system that do not pollute liquid metal sample;
- to design an easy-to-use system that complies with a nuclear environment;
- to provide a system that may be quickly cooled.

Such a device was already developed for the lead-lithium eutectic alloy that is studied for the tritium-breeding blanket of fusion reactor [Desreumaux, 1993]. The basic principle was to adapt the sampler to the LBE melt and achieve a first qualification on a static facility. The scheme and a view of this dip sampler developed for the lead-lithium alloy is provided hereafter (Figure 4.4.10) together with the LBE sample obtained [Courouau, 2002a].

Figure 4.4.10. Scheme, view of the dip sampling system, which is then hooked to a stem and immersed throughout an air lock, as well as the resulting LBE sample

The tube on the bottom part, opposite to the hole for the inlet of the melt, was necessary to ensure a good filling of the sampler by enabling degassing. This tube is not really needed for lead-bismuth alloy because of its higher density. The dip sampler fabrication could then be simplified. The stripy marks done during fabrication on the external surface of the dip sampler enable, in principle, an easy discarding of the steel, like the opening of a tin, delivering the LBE sample ready for its analysis.

The nature of the material used up to now is stainless steel. Its effect on the dissolved impurities content was not assessed. However, a material pure and presenting very low solubilities in lead alloys is recommended. Elements such as Fe, Cr, Nb, Mo, Co, Ti, Si and Zr present very low solubilities in the liquid lead-alloys eutectic, and could be efficiently used for the dip sampling material. However, as Fe and Cr are two of the impurities to be analysed, it is recommended to avoid them for the candidate material. Carbon in the form of graphite or composite like SiC can possibly be used.

The issue of the representativeness of the measurement has not been treated due to the lack of any sampling in loop operating conditions. This issue is to be further investigated, as the sampling system might not be homogeneous for all nuclides. Indeed, some impurities might be concentrated on the walls
of the sampling system, so that the conditions of sampling (temperature, immersion time, temperature
decrease gradient, etc.) are to be optimised on the basis of the future experimental feedback. In addition,
the topic of the possible contamination of the sampling system during the immersion by the free surface
oxides is not addressed. The feedback from past development should be taken into account for the
liquid metal sample optimisation, such as for instance multiple sampling systems for a larger amount
of metal sampled such as the “harp sampler” (Figure 4.4.11) [Borgstedt, 1989], and especially for a
technique and know-how developed for achieving representative sampling [Borgstedt, 1989]. The use
of alternative techniques, such as on-line distillation technique that was once studied and applied for
the liquid sodium, should be reassessed.

**Figure 4.4.11. Schematic drawing of an overflow multiple sampler for flowing alkali metals, the “harp sampler” [Borgstedt, 1989]**

1 – fittings, 2 – sampler, 3 – sampler drain pot, 4 – crucible

4.4.2.2 *Chemical analysis of lead-bismuth eutectic*

Various techniques are used for lead alloy characterisation, as follows [Desreumaux, 1998]:

- composition analysis;
- characterisation of metallic impurities;
- oxygen present in the alloy measurement;

The composition analysis techniques are based on calorimetry, surface spectroscopy analysis, or
atomic absorption spectroscopy (AAS). The calorimetric method principle is to measure the thermal
flux absorbed or produced by a sample subjected to a temperature increase. The results enable
deducing the respective reaction temperature, the eutectic and peritectic points, as well as the reaction
specific heat. But this kind of analysis is not sufficient by itself as several compositions are often
possible when referring to a phase diagram.
The surface spectroscopy analysis consists of X-ray analysis, scanning electron microscopy (SEM), or wavelength dispersive X-ray fluorescence (WDXRF). When energy dispersive X-ray spectrometer (EDS) is coupled to a scanning electron microscope, the measure of the alloys composition is possible in any point of the surface of the sample. Mean value of several points (10 at least) could be used to determine the mean composition of the alloys. The scanning electron microscope enables determining the general state of the alloys, through the study of its enriched or depleted zone. The latter method, WDXRF, enables the measurement of virtually all the periodic table (Z > 11) for concentrations above 500 µg/g [Desreumaux, 1998]. This method is thus well adapted to the alloy composition determination, but not for the measurement of impurities.

The metallic impurities analyses are achieved first by dissolution of the lead alloy, and then by the use of inductive coupled plasma/mass spectrometry (ICP/MS) or AAS. The ICP/MS method enables the measurement of a wide range of impurities such as Fe, Ni, Cr, Ag, Cd, Cu, Sn, Sb,…

The iron impurity has an isobaric interference with ArO gaseous mixture (Ar being the plasma gas) that increases the lower detection limit to 50 µg/g. For the iron impurity, the AAS technique coupled with the spiking method is then a better choice than the ICP-MS technique, resulting in a lower detection limit decreased to 5 µg/g.

For the nickel impurity, because of the contamination coming from the nickel cones of the transfer chamber of the ICP/MS apparatus, the lower detection limit is high when compared to the other impurities. There are two methods for decreasing the lower detection limit: changing the cones to platinum cones, or measuring nickel by AAS with spiking method that decreases the lower detection limit to 5 µg/g as well.

The analytical measurement of oxygen in a sample can be made by two methods [Desreumaux, 1998]. The first method is based on the reductive fusion of the sample in a graphite crucible. The resulting carbon dioxide is measured by infrared spectroscopy. This technique is used with careful calibration in the expected range, and with devoted preparation procedures for the sample in order to reduce any superficial oxide. It measures the total amount of oxygen present in the alloys: either the dissolved oxygen or the oxides. The other method is based on electrochemical measurement as described in the next subtask with laboratory scale electrochemical cells. It measures only the dissolved oxygen present in the liquid metal solution.

The methods were applied to LBE samples performed on the alloy supplied by METALEUROP to CEA Cadarache [Desreumaux, 1998] (Table 4.4.3).

<table>
<thead>
<tr>
<th>Table 4.4.3. Composition of the METALEUROP LBE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calorimetry</strong></td>
</tr>
<tr>
<td>Melting point</td>
</tr>
<tr>
<td>Measurements</td>
</tr>
</tbody>
</table>

Table 4.4.4 gives the impurities measured, as well as the values of the pure lead and bismuth characterised by the supplier for comparison. During the cooling phase of the dip sampling, a segregation phenomenon occurs, resulting in a relative heterogeneity of the lead alloy depending on the method used for composition characterisation. Typically, a better composition measurement is obtained by dissolution of the whole sample, than on parts of the sample.
Table 4.4.4. Metallic impurities measured in the METALEUROP LBE

<table>
<thead>
<tr>
<th>Analytical technique</th>
<th>EPB measured ($\mu g/g$)</th>
<th>Bi (theoretical) ($\mu g/g$)</th>
<th>Pb (theoretical) ($\mu g/g$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn ICP/MS</td>
<td>&lt;2</td>
<td>&lt;1</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Fe AAS</td>
<td>&lt;5</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>Ni AAS</td>
<td>&lt;5</td>
<td>1.4</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ag ICP/MS</td>
<td>3</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Cu ICP/MS</td>
<td>&lt;2</td>
<td>&lt;1</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Zn ICP/MS</td>
<td>&lt;2</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>Cd ICP/MS</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Sb ICP/MS</td>
<td>&lt;2</td>
<td>&lt;3</td>
<td>&lt;2</td>
</tr>
<tr>
<td>As ICP/MS</td>
<td>&lt;2</td>
<td>&lt;1</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Te ICP/MS</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;3</td>
</tr>
</tbody>
</table>

The table provides the metallic impurities concentrations measured in the alloys with the different analysis techniques. This compares well to one of the other characterisation available [Glasbrenner, 2004b] made on the LBE supplied by Impag AG (Switzerland) which contained a few ppm of impurities: Ag 11.4, Fe 0.78, Ni 0.42, Sn 13.3, Cd 2.89, Al 0.3, Cu 9.8, Zn 0.2.

The first tests for the oxygen measurement were made with a LECO apparatus calibrated with steel matrix giving thus a different fusion temperature. The results showed dispersed values for the lead alloy sample: from 1 $\mu g/g$ to 5 $\mu g/g$. A different approach based on calibration of the apparatus with a 1 $\mu g/g$ lead sample did not allow lowering the detection limit. Actually, the apparatus used for these measurements proved insufficient for this kind of study: background level of the LECO apparatus is too high and its resulting sensitivity appeared too low when compared to the effective operating oxygen concentration range (0.01 ppm).

4.4.2.3 Radioactive nuclides chemical analysis

The regular radio activation measurement of the coolant is typical for nuclear system operation, as it can affect the reactor operation (handling or repair during maintenance operation, fuel-cladding failure, transfer or accumulation on specific part of the system…). All nuclides being gamma emitters can be measured by gamma spectrometry. This is typically achieved after having dissolved the metal sample in an aqueous solution (nitric acid). However, other nuclides, which are specific to the spallation reaction, or due to the activation of the heavy liquid metal coolant, are only beta-emitters (most of the Bi, Tl, Hg, Au, Pt nuclides), or even alpha-emitters ($^{208,209,210}$Po). Their measurement requires then specific procedure in order to be able to measure traces, and in some case to be able to measure each of the isotopes produced for one particular nuclide (Po).

Preliminary investigations were achieved for the Po isotopes speciation by [Lacressonniere, 2003] that was applied to one of the first LiSoR irradiated sample (36 hours, 2002). Measurements gave: 3752 Bq/g of $^{208}$Po, 22 Bq/g of $^{209}$Po, 19 Bq/g of $^{210}$Po, which corresponds to the measurement achieved independently by the Paul Scherrer Institute [Glasbrenner, 2004b], as well as to the nuclear production assessment. The technique is based on concentration of the nuclides in a first step (ferric co-precipitation, and liquid-liquid extraction with tri-butyl-phosphate), then in a second step by the self-deposition on an argent disk for alpha-spectrometry measurement.
The technique that was under study for the traces measurement of the mercury concentration is the atomic absorption spectrometry coupled with a vapour generator. The detection limit achieved by this method is 0.06 ppm ($6 \times 10^{-9}$ g/g) [Chabert, 2003].

4.4.2.4 Conclusions

The dip sampling system that was originally developed for Pb-Li alloys got a first validation in LBE. The issue of the representation is to be further assessed, in order to eventually propose an optimised design. Indeed, the sample must be representative of the liquid metal bulk, which is depending of the location of the sampling, and then of the design of the nuclear system.

The analytical techniques for metallic impurities measurement: Fe, Ni, Cu, Sn, Ag, Zn, Cd, Sb, As, Te, for which either ICP-MS or AAS with spiking method have been used, were as well demonstrated. However, the lower detection limit of 5 ppm cannot be further lowered, unless another ICP-MS apparatus, more costly, is used to lower the detection limit by one order of magnitude: 0.5 ppm. Industrial analytical laboratories are usually equipped with such equipment. A cross-comparison benchmark with such laboratories is necessary, however, to confirm the lower detection limit and accuracy of the measurement, including, in particular all the crucial preparation steps of the samples.

Concerning the radioactive impurities, measurement techniques were developed only for the speciation of the polonium and mercury, as the techniques for low alpha or beta activities measurement are not straightforward. Further developments for the speciation methods should concern the main spallation and activation products isotopes that are expected for normal operating conditions: Po, Bi, Pb, Hg, Au, Pt, Ir, Re, Ta, Hf. The techniques for solvatation, concentration, etc., are part of the development envisaged.

However, during normal operating conditions in an anisothermal system, the equilibrium concentration of the main impurities involved in the corrosion and mass transfer processes will be lower or even far lower than the lower detection limit available (5 ppm or even 0.5 ppm). This makes really difficult the iron monitoring, for instance. There is no straight solution foreseeable to solve that issue, except the use of an indirect measurement method. Indeed, the steel making industry uses the oxygen measurement to check the dissolved carbon, as the dissolved oxygen is defined by the C/CO$_2$ chemical equilibrium in that particular condition. Detecting the iron oxide stability threshold, providing the availability of precise data and good sensor accuracy could be one of the solutions.

4.5 Conclusions

The chemistry control in a nuclear system appears as a quite complex issue, and particularly critical to keep under control the corrosion in a wider operating temperature range, as well as to keep the coolant free of any contamination by oxides, which is basically the first requirement. The radiochemistry control appears as well as difficult, as, production rates are relatively inaccurate, and as the transport phenomena as well as associated purification processes are to be more understood and developed.

However, the chemistry control is usually not critical for operation if it was taken into account at the early stage of the design as well as during the start-up and shutdown procedures. This is why it should not be neglected in designing any kind of systems, especially in the view of the potential operating difficulties that could result from it. Well-designed and well-operated facilities could be run, in principle, with a rather high confidence, in the no-oxygen conditions. Higher operating temperatures require the validation of oxygen control systems at a specified medium range concentration on the long term for larger systems, and especially for pure lead.
There are some similarities in the chemistry analysis of water, liquid sodium and lead alloy systems. They all present quite identical requirements for both monitoring and processes. However, the consequences for an LBE system are much more critical, such as the loss of cooling capacity due to plugging or the loss of confinement due to corrosion, which makes this issue as one of the most important one when operating such system.

Some points remains open for further studies, such as the process optimisation of oxygen control systems, the improvement of the reliability of the associated instrumentation, such as the oxygen sensor, as well as the basic phenomena for aerosols, particles and mass transfer, even of impurities present in traces such as the active contaminants, within a close and tight system on the long term, for which the basic understanding should be increased.

REFERENCES


Chabert, C. (2003), personal notes.


HSC Chemistry for Windows Version 4.1, Chemical reaction and equilibrium software, Outokumpu.

JANAF Thermochemical Tables.


Li, N. (2004), personal notes.


TECDOC-687 (1993), Fission and Corrosion Product Behaviour in Liquid Metal Fast Breeder Reactors (LMFBRs), IAEA.

TECDOC-1056 (1998), Nuclear Heat Applications: Design Aspects and Operating Experience, IAEA.

TECDOC-1289 (2002), Comparative Assessment of Thermophysical and Thermohydraulic Characteristics of Lead, Lead-bismuth, and Sodium Coolants for Fast Reactors, IAEA.

TECDOC-1348 (2003), Power Reactors and Sub-critical Blanket Systems with Lead and Lead-bismuth as Coolant and/or Target Material, IAEA.


Chapter 5
PROPERTIES OF IRRADIATED LBE AND Pb

5.1 Introduction

Lead and LBE possess favourable properties as both a spallation neutron target material and as a coolant for ADS and reactor systems. For ADS applications, these properties include: 1) a high yield of about 28 n for LBE and 24 n for Pb per 1 GeV proton; 2) both melts have an extremely small neutron absorption cross-section; (3) a small scattering cross-section [Gudowski, 2000]. As a coolant, lead and LBE possess: 1) high boiling points; 2) high heat capacities; (3) inert behaviour with respect to reaction with water.

For safe operation and post-irradiation handling of LBE and Pb it is necessary to know the nuclides generated during irradiation. Some of these nuclides are volatile, hazardous and rather long-lived. Their behaviour within the system is strongly influenced by the environment including the oxygen content and temperature. If volatiles are produced, their release rates under specific conditions must be evaluated. The release of volatiles may be prevented by the application of a suitable absorber.

Protons of 600 MeV energy induce spallation reactions in heavy materials such as Pb and Bi. These reactions generate direct spallation products, consisting of nuclei with masses close to that of the target nuclei. At the high energies involved multiple inelastic reactions are possible. Therefore, one must expect a large number of isotopes as products. For instance, reactions on Pb generate Hg isotopes roughly from $^{180}$Hg to $^{206}$Hg.

Similarly, reactions of protons on Bi generate Po isotopes up to $^{209}$Po. $^{210}$Po is generated by neutron capture on $^{209}$Bi, and subsequent β decay of the compound nucleus $^{210}$Bi. Neutron capture of course exist for all the isotopes with a high capture cross-section, not only for $^{209}$Bi. Another source of Po in pure Pb systems is the production of $^{209}$Pb from $^{208}$Pb followed by β− decay to $^{209}$Bi. Po production then proceeds as described above by neutron capture to form $^{210}$Bi and β− decay. In critical systems such as the Lead Fast Reactor (LFR), Po production is a serious issue when LBE is the coolant due to the direct production from Bi. However, it is also a concern in Pb-cooled systems due to the multi-step reaction beginning with $^{208}$Pb as described above. Other direct products of high energy reactions include light particles, such as $^3$He, hydrogen and tritium. Also fissions are induced by high energy protons as well as thermal and fast neutrons. Fission products are lighter elements, and include for instance I, Ar, Kr, Xe and so on. In particular, halogen containing species, iodine compounds for example, will also be important since they may be volatile.

The influence of protons with energies of 590 MeV [Pitcher, 2002], [Foucher, 2002], [Zanini, 2005] and 72 MeV [Foucher, 2002] to LBE were calculated with Monte Carlo programs and it was shown that the full spectrum of isotopes (light, medium and heavy elements) are generated during the

* Chapter lead: Heike Glasbrenner (PSI, Switzerland). For additional contributors, please see the List of Contributors included at the end of this work.
irradiation process in an ADS system. Since the most hazardous isotopes (Po, Hg) are produced directly from the major components in LBE, a detailed specification that includes the concentrations of contaminants has not been specified for nuclear systems.

In the following chapter theoretical considerations concerning the formation and behaviour of polonium and iodine are discussed. Thermodynamic properties of polonium are derived in an extrapolative manner from its group homologous. In a similar way, thermodynamic properties of some polonium compounds important for LBE systems are derived. The interaction of polonium with metals in the condensed phase is treated using the semi-empirical Miedema model [de Boer, 1988]. Some results achieved by irradiation experiments of LBE and subsequent investigation are presented. Selective isotopes have been generated in LBE and their evaporation and absorption behaviour investigated. The release of volatiles from a liquid LBE target was studied on-line in an experiment at CERN-ISOLDE. These results are also presented and discussed.

5.2 Theoretical considerations

5.2.1 Evaporation characteristics of polonium

Thermodynamic constants that describe the evaporation processes of polonium are summarised and critically discussed by Eichler [Eichler, 2002]. Additionally, systematic changes of the properties of the chalcogenes are analysed, empirical correlations are proposed and cyclic processes are balanced. Accordingly, the existing values of entropies for polonium are acceptable. Questionable, however, are those values of enthalpies, which have been deduced from results of the experimental investigations of the vapour pressure temperature dependency, of the melting point, and of the boiling temperatures. Technical difficulties and possible error sources of the measurements resulting from the radioactive decay properties of $^{210}$Po are discussed. Using extrapolative standard enthalpies and entropies as well as their temperature dependency, shown in Tables 5.2.1-5.2.3 [Eichler, 2002], empirical correlations for the equilibrium partial pressure of monomeric and dimeric polonium above the pure condensed phase and the equilibrium constant of the dimerisation reaction in the gas phase are as follows:

$$\log p(Po(g))/Pa = \left[11.797 \pm 0.024\right] - \left[9883.4 \pm 9.5\right]/T; T = 298-600\ K$$  \hspace{1cm} (5.1)

$$\log p(Po(g))/Pa = \left[10.661 \pm 0.057\right] - \left[9328.4 \pm 4.9\right]/T; T = 500-1300\ K$$  \hspace{1cm} (5.2)

$$\log p(Po_2(g))/Pa = \left[13.698 \pm 0.049\right] - \left[8592.3 \pm 19.6\right]/T; T = 298-600\ K$$  \hspace{1cm} (5.3)

$$\log p(Po_2(g))/Pa = \left[11.424 \pm 0.124\right] - \left[7584.1 \pm 98.1\right]/T; T = 500-1300\ K$$  \hspace{1cm} (5.4)

$$\log K_d = (-4.895 \pm 0.012) + (11071 \pm 6)/T$$  \hspace{1cm} (5.5)

with $p$ as pressure in Pa, $T$ the temperature in K and $K_d$ the equilibrium constant of the dimerisation reaction $K_d = (Po_2(g))/p(Po(g))^2$.

Figure 5.2.1 shows plots of the above empirical correlations [Eichler, 2002] together with experimental data determined by [Abakumov, 1974], [Brooks, 1955], [Ausländer, 1955] and [Beamer, 1946]. According to the extrapolations, the dominant gas phase species of polonium in the entire temperature range between 298 and 1300 K should be dimeric polonium. Experimental evidence on the actual gas phase species present, or the ratio of monomeric and diatomic polonium in the gas phase, is not available. All experimental vapour pressure measurements were performed using $^{210}$Po. These measurements are inevitably influenced by effects such as self heating of $^{210}$Po by decay heat and sputtering, thus giving rise to erroneous results especially at low temperatures. Hence, extrapolated
“latent heats” of the volatilisation processes are clearly larger compared to literature data. Especially in the temperature range of solid polonium the calculated vapour pressure curve shifts significantly to lower values, whereas the boiling point was almost reproduced by the calculation. For a critical discussion of the literature data see [Eichler, 2002].

Table 5.2.1. Temperature dependent standard entropies (Jmol⁻¹K⁻¹) and standard enthalpies (kJmol⁻¹) of polonium (selected extrapolation results) [Eichler, 2002]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>SₚPo(g)</th>
<th>H₂Po(g)</th>
<th>SₚPo(l)</th>
<th>H₂Po(l)</th>
<th>SₚPo(s)</th>
<th>H₂Po(s)</th>
<th>SₚPo2(g)</th>
<th>H₂Po2(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>187.15</td>
<td>188.9</td>
<td>–</td>
<td>–</td>
<td>55.20</td>
<td>0.00</td>
<td>282.24</td>
<td>166.2</td>
</tr>
<tr>
<td>300</td>
<td>187.28</td>
<td>188.9</td>
<td>–</td>
<td>–</td>
<td>55.36</td>
<td>0.05</td>
<td>282.49</td>
<td>166.3</td>
</tr>
<tr>
<td>400</td>
<td>193.20</td>
<td>190.9</td>
<td>–</td>
<td>–</td>
<td>66.16</td>
<td>2.74</td>
<td>294.22</td>
<td>170.4</td>
</tr>
<tr>
<td>500</td>
<td>197.89</td>
<td>192.9</td>
<td>96.13</td>
<td>16.88</td>
<td>69.68</td>
<td>5.75</td>
<td>303.40</td>
<td>174.5</td>
</tr>
<tr>
<td>600</td>
<td>201.75</td>
<td>194.9</td>
<td>99.97</td>
<td>20.38</td>
<td>75.39</td>
<td>8.94</td>
<td>310.98</td>
<td>178.7</td>
</tr>
<tr>
<td>700</td>
<td>205.06</td>
<td>197.0</td>
<td>104.08</td>
<td>24.51</td>
<td>80.54</td>
<td>12.36</td>
<td>317.47</td>
<td>182.9</td>
</tr>
<tr>
<td>800</td>
<td>207.36</td>
<td>199.1</td>
<td>107.94</td>
<td>28.36</td>
<td>–</td>
<td>–</td>
<td>323.15</td>
<td>187.1</td>
</tr>
<tr>
<td>900</td>
<td>210.52</td>
<td>201.3</td>
<td>111.94</td>
<td>32.06</td>
<td>–</td>
<td>–</td>
<td>328.22</td>
<td>191.4</td>
</tr>
<tr>
<td>1000</td>
<td>212.89</td>
<td>203.4</td>
<td>115.20</td>
<td>35.83</td>
<td>–</td>
<td>–</td>
<td>332.80</td>
<td>195.8</td>
</tr>
<tr>
<td>1100</td>
<td>215.02</td>
<td>205.6</td>
<td>118.20</td>
<td>39.60</td>
<td>–</td>
<td>–</td>
<td>337.00</td>
<td>200.2</td>
</tr>
<tr>
<td>1200</td>
<td>217.00</td>
<td>207.9</td>
<td>120.85</td>
<td>43.37</td>
<td>–</td>
<td>–</td>
<td>340.88</td>
<td>204.7</td>
</tr>
<tr>
<td>1300</td>
<td>218.83</td>
<td>210.1</td>
<td>123.22</td>
<td>46.37</td>
<td>–</td>
<td>–</td>
<td>344.49</td>
<td>209.2</td>
</tr>
</tbody>
</table>

Table 5.2.2. Temperature dependence of standard entropy of polonium (extrapolation)

Standard entropy: Sₜ = A + BT + CT² + DT³ [Eichler 2002]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>SₚPo(g) ± Δ</th>
<th>H₂Po(g) ± Δ</th>
<th>SₚPo(l) ± Δ</th>
<th>H₂Po(l) ± Δ</th>
<th>SₚPo(s) ± Δ</th>
<th>H₂Po(s) ± Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>164.30495</td>
<td>0.708</td>
<td>0.0947</td>
<td>4.60499*10⁻⁶</td>
<td>1.89789*10⁻⁸</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>78.25652</td>
<td>2.40963</td>
<td>0.02762</td>
<td>2.25857*10⁻⁵</td>
<td>-1.32887*10⁻⁸</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>21.06849</td>
<td>0.51653</td>
<td>0.14888</td>
<td>2.17107*10⁻⁶</td>
<td>5.96463*10⁻⁸</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>2.0961</td>
<td>0.1811</td>
<td>0.18734</td>
<td>-1.29537*10⁻⁸</td>
<td>3.78409*10⁻⁸</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2.3. Temperature dependence of standard enthalpy of polonium (extrapolation)

Standard enthalpy: Hₜ = A + BT + CT² + DT³ [Eichler 2002]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>H₂Po(g) ± Δ</th>
<th>H₂Po(l) ± Δ</th>
<th>H₂Po(s) ± Δ</th>
<th>H₂Po2(g) ± Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>183.22359</td>
<td>0.01493</td>
<td>0.01829</td>
<td>7.01599*10⁻⁵</td>
</tr>
<tr>
<td>300</td>
<td>2.33896*10⁻⁵</td>
<td>0.00255</td>
<td>2.15156*10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>-5.97236</td>
<td>0.13768</td>
<td>2.33896*10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>2.0991</td>
<td>0.02024</td>
<td>2.33896*10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>-5.97236</td>
<td>0.13768</td>
<td>2.33896*10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>154.42684</td>
<td>0.03892</td>
<td>2.44905*10⁻⁶</td>
<td></td>
</tr>
</tbody>
</table>

181
The results of the extrapolation for the standard enthalpy of the gaseous monomeric polonium and the dimerisation enthalpy are:

$$\Delta H_{298}^0 \text{Po (g)} = 188.9 \text{ kJ/mol and } \Delta H_{298}^0 \text{ (form) Po}_2 (g) = 211.5 \text{ kJ/mol}$$

The preferred evaporation of pure polonium in the dimeric state requires new interpretations of the thermodynamic relations of polonium in mixed phases (activity coefficients), if the experimental conditions exclude a formation of the dimers due to low concentrations.

The thermodynamic data derived by extrapolation [Eichler, 2002], while not highly accurate, at least represent a consistent set of data. To acquire more reliable data, that are essential for the prediction of polonium behaviour in a technical system, experimental thermodynamic studies using polonium isotopes which are less prone to radiation effects, such as $^{209}\text{Po}$, are definitely necessary.

5.2.2 Volatilisation pathways of polonium

An analysis of the literature data for the thermochemical constants of polonium shows substantial deviations in the relations of these constants among each other, as well as in the expected trends of these constants within the chalcogen group [Eichler, 2002]. This fact considerably complicates the assessment of possible release paths for polonium from a lead-bismuth spallation target or critical system and reduces the reliability of predictions and estimations.

For elemental polonium, a coherent set of thermodynamic data was extrapolated and critically discussed in [Eichler, 2002] (see Section 5.2.1). For polonium compounds, almost no experimental thermodynamic data are available. Therefore, as a first step, a coherent set of thermodynamic data for polonium hydride, lead polonide and polonium dioxide was derived using extrapolative procedures by Eichler, et al. [Eichler, 2004a]. Using these data, the equilibrium constants of formation, dissociation and evaporation reactions were calculated. Furthermore, equilibrium constants for the reactions of lead polonide and polonium dioxide with hydrogen, water vapour as well as with lead and bismuth were
evaluated. It has to be pointed out that such extrapolations do not give results of high accuracy. Precise measurements of thermodynamic data of polonium compounds that would be required for engineering purposes are scarce. Thus, the extrapolated data can be considered as best available estimates. Detailed experimental studies of the discussed systems, preferably using $^{209}$Po are strongly recommended.

Based on the results of extrapolations, possible volatilisation processes are evaluated. From this assessment, volatilisation of polonium most likely occurs in form of diatomic polonium molecules or as diatomic intermetallic molecules. Rates for the release of radioactivity and their temperature dependency have been calculated. The main results of this study are summarised in the following section.

For the entropy of polonium hydride the following temperature function is recommended:

\[ S_{T}^{\text{H}_2\text{Po}(g)} = \left( \frac{206.07678 \pm 1.41 \times 10^3}{T} \right) + \left( \frac{0.12098 \pm 0.00437 \times 10^3}{T} \right) - \left( 3.73042 \times 10^{-5} \right) \times T^2 \]  

(5.7)

Entropy values for polonium hydride together with those of polonium and hydrogen are compiled in Table 5.2.4.

Calculated entropy of formation values for polonium hydride are compiled in Table 5.2.5 for the six different formation reactions given below [Eqs. (5.8) to (5.13)]. The corresponding enthalpy and Gibbs free energy values are given in Tables 5.2.6 and 5.2.7.

For polonium hydride:

- $\text{Po (cond)} + \text{H}_2(g) \rightleftharpoons \text{H}_2\text{Po}(g)$
- $\text{Po (g)} + \text{H}_2(g) \rightleftharpoons \text{H}_2\text{Po}(g)$
- $0.5 \text{Po}_2(g) + \text{H}_2(g) \rightleftharpoons \text{H}_2\text{Po}(g)$
- $\text{Po (cond)} + 2\text{H}(g) \rightleftharpoons \text{H}_2\text{Po}(g)$
- $\text{Po (g)} + 2\text{H}(g) \rightleftharpoons \text{H}_2\text{Po}(g)$
- $0.5 \text{Po}_2(g) + 2\text{H}(g) \rightleftharpoons \text{H}_2\text{Po}(g)$

Table 5.2.4. Standard entropies of gaseous polonium hydride, dimeric and monoatomic gaseous polonium and hydrogen

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$S_T^{\text{H}_2\text{Po}(g)}$ (Jmol$^{-1}$K$^{-1}$)</th>
<th>$S_T^{\text{Po(sld)}}$ (Jmol$^{-1}$K$^{-1}$) [Eichler, 2002]</th>
<th>$S_T^{\text{Po}(g)}$ (Jmol$^{-1}$K$^{-1}$) [Eichler, 2002]</th>
<th>$S_T^{\text{Po}_2(g)}$ (Jmol$^{-1}$K$^{-1}$) [Eichler, 2002]</th>
<th>$S_T^{\text{H}_2(g)}$ (Jmol$^{-1}$K$^{-1}$) [Barin, 1995]</th>
<th>$S_T^{\text{H}(g)}$ (Jmol$^{-1}$K$^{-1}$) [Barin, 1995]</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>238.13</td>
<td>55.20</td>
<td>187.13</td>
<td>282.24</td>
<td>130.68</td>
<td>114.716</td>
</tr>
<tr>
<td>300</td>
<td>238.35</td>
<td>55.36</td>
<td>187.28</td>
<td>282.49</td>
<td>130.86</td>
<td>114.845</td>
</tr>
<tr>
<td>400</td>
<td>249.49</td>
<td>63.16</td>
<td>193.20</td>
<td>294.22</td>
<td>139.22</td>
<td>120.824</td>
</tr>
<tr>
<td>500</td>
<td>258.09</td>
<td>69.68</td>
<td>197.89</td>
<td>303.40</td>
<td>145.74</td>
<td>125.463</td>
</tr>
<tr>
<td>600</td>
<td>265.76</td>
<td>99.97</td>
<td>201.75</td>
<td>310.98</td>
<td>151.08</td>
<td>129.252</td>
</tr>
<tr>
<td>700</td>
<td>272.51</td>
<td>104.08</td>
<td>205.06</td>
<td>317.47</td>
<td>155.61</td>
<td>132.457</td>
</tr>
<tr>
<td>800</td>
<td>278.56</td>
<td>107.94</td>
<td>208.00</td>
<td>323.15</td>
<td>159.55</td>
<td>135.232</td>
</tr>
<tr>
<td>900</td>
<td>284.07</td>
<td>111.94</td>
<td>210.52</td>
<td>328.22</td>
<td>163.05</td>
<td>137.680</td>
</tr>
<tr>
<td>1000</td>
<td>289.15</td>
<td>115.20</td>
<td>212.88</td>
<td>332.8</td>
<td>166.22</td>
<td>139.870</td>
</tr>
<tr>
<td>1100</td>
<td>293.88</td>
<td>118.2</td>
<td>215.02</td>
<td>337.00</td>
<td>169.11</td>
<td>141.851</td>
</tr>
<tr>
<td>1200</td>
<td>298.31</td>
<td>120.85</td>
<td>216.99</td>
<td>340.88</td>
<td>171.79</td>
<td>143.660</td>
</tr>
</tbody>
</table>
Table 5.2.5. Entropy of polonium hydride formation for different reactions

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta S_{T,\text{form}H_2Po(g)}$ (J mol$^{-1}$ K$^{-1}$) Eq. (5.8)</th>
<th>$\Delta S_{T,\text{form}H_2Po(g)}$ (J mol$^{-1}$ K$^{-1}$) Eq. (5.9)</th>
<th>$\Delta S_{T,\text{form}H_2Po(g)}$ (J mol$^{-1}$ K$^{-1}$) Eq. (5.10)</th>
<th>$\Delta S_{T,\text{form}H_2Po(g)}$ (J mol$^{-1}$ K$^{-1}$) Eq. (5.11)</th>
<th>$\Delta S_{T,\text{form}H_2Po(g)}$ (J mol$^{-1}$ K$^{-1}$) Eq. (5.12)</th>
<th>$\Delta S_{T,\text{form}H_2Po(g)}$ (J mol$^{-1}$ K$^{-1}$) Eq. (5.13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>52.25</td>
<td>-79.68</td>
<td>-33.67</td>
<td>-46.50</td>
<td>-178.43</td>
<td>-132.42</td>
</tr>
<tr>
<td>300</td>
<td>52.13</td>
<td>-79.79</td>
<td>-33.76</td>
<td>-46.70</td>
<td>-178.62</td>
<td>-132.59</td>
</tr>
<tr>
<td>400</td>
<td>47.11</td>
<td>-89.23</td>
<td>-36.84</td>
<td>-55.32</td>
<td>-185.36</td>
<td>-139.27</td>
</tr>
<tr>
<td>500</td>
<td>42.67</td>
<td>-85.54</td>
<td>-39.35</td>
<td>-62.52</td>
<td>-190.73</td>
<td>-144.54</td>
</tr>
<tr>
<td>600</td>
<td>14.71</td>
<td>-87.07</td>
<td>-40.81</td>
<td>-79.71</td>
<td>-194.49</td>
<td>-148.23</td>
</tr>
<tr>
<td>700</td>
<td>12.82</td>
<td>-88.16</td>
<td>-41.84</td>
<td>-96.48</td>
<td>-197.46</td>
<td>-151.14</td>
</tr>
<tr>
<td>800</td>
<td>11.07</td>
<td>-89.99</td>
<td>-42.09</td>
<td>-99.84</td>
<td>-199.01</td>
<td>-153.48</td>
</tr>
<tr>
<td>900</td>
<td>9.08</td>
<td>-89.5</td>
<td>-42.57</td>
<td>-103.23</td>
<td>-201.81</td>
<td>-155.40</td>
</tr>
<tr>
<td>1000</td>
<td>7.73</td>
<td>-89.95</td>
<td>-44.37</td>
<td>-105.79</td>
<td>-203.47</td>
<td>-156.99</td>
</tr>
<tr>
<td>1100</td>
<td>6.57</td>
<td>-90.25</td>
<td>-43.73</td>
<td>-108.02</td>
<td>-204.73</td>
<td>-158.32</td>
</tr>
<tr>
<td>1200</td>
<td>5.67</td>
<td>-90.47</td>
<td>-43.92</td>
<td>-109.86</td>
<td>-206.00</td>
<td>-159.45</td>
</tr>
</tbody>
</table>

Table 5.2.6. Standard formation enthalpy for polonium hydride and enthalpies for its formation from the elements in different states [Reactions (5.8) to (5.13)]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta H_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.8)</th>
<th>$\Delta H_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.9)</th>
<th>$\Delta H_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.10)</th>
<th>$\Delta H_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.11)</th>
<th>$\Delta H_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.12)</th>
<th>$\Delta H_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>163.0</td>
<td>-25.9</td>
<td>79.9</td>
<td>-273.0</td>
<td>-461.9</td>
<td>-356.1</td>
</tr>
<tr>
<td>300</td>
<td>165.9</td>
<td>-22.9</td>
<td>82.8</td>
<td>-270.1</td>
<td>-459.0</td>
<td>-353.2</td>
</tr>
<tr>
<td>400</td>
<td>164.9</td>
<td>-23.2</td>
<td>82.5</td>
<td>-272.3</td>
<td>-460.5</td>
<td>-354.8</td>
</tr>
<tr>
<td>500</td>
<td>166.2</td>
<td>-20.9</td>
<td>84.7</td>
<td>-272.2</td>
<td>-459.4</td>
<td>-353.7</td>
</tr>
<tr>
<td>600</td>
<td>152.0</td>
<td>-22.6</td>
<td>83.0</td>
<td>-187.8</td>
<td>-462.3</td>
<td>-356.8</td>
</tr>
<tr>
<td>700</td>
<td>149.1</td>
<td>-23.4</td>
<td>82.2</td>
<td>-291.8</td>
<td>-464.3</td>
<td>-358.8</td>
</tr>
<tr>
<td>800</td>
<td>146.7</td>
<td>-24.0</td>
<td>81.5</td>
<td>-295.4</td>
<td>-466.2</td>
<td>-360.6</td>
</tr>
<tr>
<td>900</td>
<td>144.6</td>
<td>-24.6</td>
<td>81.0</td>
<td>-298.7</td>
<td>-468.0</td>
<td>-362.4</td>
</tr>
<tr>
<td>1000</td>
<td>141.9</td>
<td>-25.7</td>
<td>79.8</td>
<td>-302.6</td>
<td>-470.2</td>
<td>-364.7</td>
</tr>
<tr>
<td>1100</td>
<td>140.4</td>
<td>-25.6</td>
<td>79.9</td>
<td>-305.2</td>
<td>-471.2</td>
<td>-365.7</td>
</tr>
<tr>
<td>1200</td>
<td>137.6</td>
<td>-27.0</td>
<td>78.6</td>
<td>-309.1</td>
<td>-473.7</td>
<td>-368.1</td>
</tr>
</tbody>
</table>

Table 5.2.7. Temperature dependency of Gibbs free energy values for polonium hydride formation [Eqs. (5.8) to (5.13)]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta G_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.8)</th>
<th>$\Delta G_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.9)</th>
<th>$\Delta G_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.10)</th>
<th>$\Delta G_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.11)</th>
<th>$\Delta G_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.12)</th>
<th>$\Delta G_{T,\text{form}H_2Po(g)}$ (kJ mol$^{-1}$) Eq. (5.13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>147.4</td>
<td>-2.2</td>
<td>89.9</td>
<td>-259.2</td>
<td>-408.8</td>
<td>-316.7</td>
</tr>
<tr>
<td>300</td>
<td>150.0</td>
<td>1.0</td>
<td>92.9</td>
<td>-256.2</td>
<td>-405.5</td>
<td>-313.5</td>
</tr>
<tr>
<td>400</td>
<td>146.1</td>
<td>10.0</td>
<td>97.2</td>
<td>-254.5</td>
<td>-390.6</td>
<td>-303.3</td>
</tr>
<tr>
<td>500</td>
<td>144.9</td>
<td>21.9</td>
<td>104.4</td>
<td>-249.4</td>
<td>-372.4</td>
<td>-289.8</td>
</tr>
<tr>
<td>600</td>
<td>143.1</td>
<td>29.7</td>
<td>107.5</td>
<td>-244.7</td>
<td>-358.2</td>
<td>-280.4</td>
</tr>
<tr>
<td>700</td>
<td>140.1</td>
<td>38.3</td>
<td>111.5</td>
<td>-241.0</td>
<td>-342.8</td>
<td>-269.7</td>
</tr>
<tr>
<td>800</td>
<td>137.9</td>
<td>47.2</td>
<td>115.6</td>
<td>-236.4</td>
<td>-327.1</td>
<td>-258.7</td>
</tr>
<tr>
<td>900</td>
<td>136.4</td>
<td>55.9</td>
<td>119.7</td>
<td>-230.9</td>
<td>-311.4</td>
<td>-247.5</td>
</tr>
<tr>
<td>1000</td>
<td>134.1</td>
<td>64.2</td>
<td>123.3</td>
<td>-226.0</td>
<td>-295.9</td>
<td>-236.9</td>
</tr>
<tr>
<td>1100</td>
<td>133.2</td>
<td>73.7</td>
<td>128.0</td>
<td>-219.7</td>
<td>-279.2</td>
<td>-224.9</td>
</tr>
<tr>
<td>1200</td>
<td>130.8</td>
<td>81.6</td>
<td>131.3</td>
<td>-214.8</td>
<td>-263.9</td>
<td>-214.3</td>
</tr>
</tbody>
</table>
The following temperature functions have been derived from Tables 5.2.8 and 5.2.9 for the entropy of gaseous and solid lead polonide [Eichler, 2004a]:

$$S_T \text{ PbPo (g)} = 233.2798 + 0.19892 T - 1.5756 \times 10^{-4} T^2 + 5.19651 \times 10^{-8} T^3$$ (5.14)

$$S_T \text{ PbPo (s)} = 53.19976 + 0.27136 T - 2.1165 \times 10^{-4} T^2 + 7.16652 \times 10^{-8} T^3$$ (5.15)

This results in the following relation for the entropy of sublimation:

$$\Delta S_T (\text{subl}) \text{ PbPo} = 180.08004 - 0.07244 T + 5.40902 \times 10^{-5} T^2 - 1.97001 \times 10^{-8} T^3$$ (5.16)

Entropy and enthalpy values for PbPo are compiled in Tables 5.2.8 and 5.2.9 together with the entropy of sublimation and the entropies of formation of gaseous and solid PbPo from the elements in their standard state at the given temperature. Gibbs free energy values for these formation reactions as well as the sublimation reaction are listed in Table 5.2.10 together with the corresponding equilibrium constants or vapour pressures, respectively.

Extrapolated entropy values for polonium dioxide are given in Table 5.2.11 together with its entropy of sublimation and formation.

Enthalpy data have been extrapolated for the formation of gaseous and solid polonium dioxide from the gaseous monoatomic elements, i.e. oxygen and polonium. These values are compiled in Table 5.2.12 together with the resulting values for enthalpy of sublimation and vapour pressure. The derived enthalpy values should be regarded cautiously because they are based on rather few literature data for chalcogen dioxides (SeO$_2$ and TeO$_2$) and the chemical bonding in these compounds (polar covalent) differs substantially from the bonding in PoO$_2$ (partially ionic).

Table 5.2.8. Extrapolated entropy values of gaseous and solid lead polonide, sublimation entropy of PbPo and entropies for the formation of gaseous and solid PbPo from the elements in their standard state [Eichler, 2004a]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$S_T$ (g) $\text{Jmol}^{-1}\text{K}^{-1}$</th>
<th>$S_T$ (s) $\text{Jmol}^{-1}\text{K}^{-1}$</th>
<th>$\Delta S$ (subl) $\text{Jmol}^{-1}\text{K}^{-1}$</th>
<th>$\Delta S$ (form) PbPo (g) $\text{Jmol}^{-1}\text{K}^{-1}$</th>
<th>$\Delta S$ (form) PbPo (s) $\text{Jmol}^{-1}\text{K}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>285.46</td>
<td>122.61</td>
<td>162.854</td>
<td>159.919</td>
<td>-2.941</td>
</tr>
<tr>
<td>300</td>
<td>285.57</td>
<td>122.92</td>
<td>162.651</td>
<td>159.722</td>
<td>-2.918</td>
</tr>
<tr>
<td>400</td>
<td>295.25</td>
<td>137.87</td>
<td>157.383</td>
<td>152.441</td>
<td>-6.139</td>
</tr>
<tr>
<td>500</td>
<td>304.85</td>
<td>149.72</td>
<td>155.130</td>
<td>150.807</td>
<td>-3.720</td>
</tr>
<tr>
<td>600</td>
<td>311.69</td>
<td>159.62</td>
<td>152.067</td>
<td>122.927</td>
<td>-29.143</td>
</tr>
<tr>
<td>700</td>
<td>317.46</td>
<td>168.19</td>
<td>149.273</td>
<td>112.128</td>
<td>-37.115</td>
</tr>
<tr>
<td>800</td>
<td>322.45</td>
<td>175.77</td>
<td>146.683</td>
<td>108.771</td>
<td>-37.911</td>
</tr>
<tr>
<td>900</td>
<td>326.84</td>
<td>182.60</td>
<td>144.245</td>
<td>106.330</td>
<td>-37.910</td>
</tr>
<tr>
<td>1000</td>
<td>330.77</td>
<td>188.84</td>
<td>141.930</td>
<td>103.989</td>
<td>-37.940</td>
</tr>
<tr>
<td>1100</td>
<td>334.31</td>
<td>194.60</td>
<td>139.715</td>
<td>101.814</td>
<td>-37.900</td>
</tr>
</tbody>
</table>
Table 5.2.9. Extrapolated enthalpy values of gaseous and solid lead polonide, sublimation enthalpy of PbPo and enthalpies for the formation of gaseous and solid PbPo from the elements in their standard state [Eichler, 2004a]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>H\text{r} PbPo (g) (kJmol(^{-1}))</th>
<th>H\text{r} PbPo (s) (kJmol(^{-1}))</th>
<th>ΔH\text{r} (subl) PbPo (kJmol(^{-1}))</th>
<th>ΔH\text{r} (form) PbPo (g) (kJmol(^{-1}))</th>
<th>ΔH\text{r} (form) PbPo (s) (kJmol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>184.2</td>
<td>-35.43</td>
<td>219.6</td>
<td>184.20</td>
<td>-35.43</td>
</tr>
<tr>
<td>300</td>
<td>183.7</td>
<td>-35.25</td>
<td>218.9</td>
<td>183.55</td>
<td>-35.36</td>
</tr>
<tr>
<td>400</td>
<td>186.6</td>
<td>-30.14</td>
<td>216.7</td>
<td>181.07</td>
<td>-35.66</td>
</tr>
<tr>
<td>500</td>
<td>190.4</td>
<td>-25.26</td>
<td>215.7</td>
<td>179.05</td>
<td>-36.60</td>
</tr>
<tr>
<td>600</td>
<td>195.1</td>
<td>-18.97</td>
<td>214.1</td>
<td>166.20</td>
<td>-47.84</td>
</tr>
<tr>
<td>700</td>
<td>199.7</td>
<td>-12.61</td>
<td>212.3</td>
<td>158.90</td>
<td>-54.33</td>
</tr>
<tr>
<td>800</td>
<td>204.0</td>
<td>-6.47</td>
<td>210.5</td>
<td>156.31</td>
<td>-54.16</td>
</tr>
<tr>
<td>900</td>
<td>208.3</td>
<td>-0.14</td>
<td>208.5</td>
<td>153.96</td>
<td>-54.51</td>
</tr>
<tr>
<td>1000</td>
<td>212.4</td>
<td>5.93</td>
<td>206.5</td>
<td>151.34</td>
<td>-55.17</td>
</tr>
<tr>
<td>1100</td>
<td>217.1</td>
<td>12.13</td>
<td>204.9</td>
<td>149.26</td>
<td>-55.66</td>
</tr>
</tbody>
</table>

Table 5.2.10. Gibbs free energy for the formation and sublimation reactions of lead polonide and the corresponding equilibrium constants [Eichler, 2004a]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔG (form) PbPo (s) (kJmol(^{-1}))</th>
<th>lg K\text{form}</th>
<th>ΔG (form) PbPo (g) (kJmol(^{-1}))</th>
<th>lg K\text{form}</th>
<th>ΔG (subl) PbPo (s) (kJmol(^{-1}))</th>
<th>lg p\text{PbPo} p/(bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-34.55</td>
<td>6.055</td>
<td>136.54</td>
<td>-23.931</td>
<td>171.09</td>
<td>-29.986</td>
</tr>
<tr>
<td>300</td>
<td>-34.48</td>
<td>6.003</td>
<td>135.63</td>
<td>-23.613</td>
<td>170.12</td>
<td>-29.616</td>
</tr>
<tr>
<td>400</td>
<td>-33.21</td>
<td>4.336</td>
<td>120.094</td>
<td>-15.680</td>
<td>153.30</td>
<td>-20.017</td>
</tr>
<tr>
<td>500</td>
<td>-33.744</td>
<td>3.629</td>
<td>103.65</td>
<td>-10.826</td>
<td>138.39</td>
<td>-14.455</td>
</tr>
<tr>
<td>600</td>
<td>-30.35</td>
<td>2.642</td>
<td>92.44</td>
<td>-8.047</td>
<td>122.80</td>
<td>-10.689</td>
</tr>
<tr>
<td>700</td>
<td>-27.45</td>
<td>2.048</td>
<td>80.41</td>
<td>-5.999</td>
<td>107.86</td>
<td>-8.047</td>
</tr>
<tr>
<td>800</td>
<td>-22.83</td>
<td>1.490</td>
<td>69.29</td>
<td>-4.524</td>
<td>92.12</td>
<td>-6.014</td>
</tr>
<tr>
<td>900</td>
<td>-20.39</td>
<td>1.183</td>
<td>58.26</td>
<td>-3.381</td>
<td>78.654</td>
<td>-4.564</td>
</tr>
<tr>
<td>1000</td>
<td>-17.23</td>
<td>0.899</td>
<td>47.35</td>
<td>-2.473</td>
<td>64.58</td>
<td>-3.373</td>
</tr>
<tr>
<td>1100</td>
<td>-13.97</td>
<td>0.663</td>
<td>37.26</td>
<td>-1.769</td>
<td>51.23</td>
<td>-2.433</td>
</tr>
</tbody>
</table>

Table 5.2.11. Temperature dependence of the entropy of polonium dioxide

Sublimation entropy of PoO\(_2\) and entropy of formation for gaseous and solid PoO\(_2\) [Eichler, 2004a]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>S\text{T} PoO(_2) (g) (Jmol(^{-1})K(^{-1}))</th>
<th>S\text{T} PoO(_2) (s) (Jmol(^{-1})K(^{-1}))</th>
<th>ΔS\text{T} (subl) PoO(_2) (Jmol(^{-1})K(^{-1}))</th>
<th>ΔS\text{T} (form) PoO(_2) (g) (Jmol(^{-1})K(^{-1}))</th>
<th>ΔS\text{T} (form) PoO(_2) (s) (Jmol(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>286.29</td>
<td>82.41</td>
<td>203.89</td>
<td>25.945</td>
<td>-177.94</td>
</tr>
<tr>
<td>300</td>
<td>286.57</td>
<td>82.84</td>
<td>203.73</td>
<td>25.878</td>
<td>-177.85</td>
</tr>
<tr>
<td>400</td>
<td>300.47</td>
<td>103.07</td>
<td>197.40</td>
<td>23.439</td>
<td>-173.96</td>
</tr>
<tr>
<td>500</td>
<td>312.20</td>
<td>118.45</td>
<td>193.76</td>
<td>21.83</td>
<td>-171.93</td>
</tr>
<tr>
<td>600</td>
<td>322.09</td>
<td>130.60</td>
<td>191.50</td>
<td>-4.327</td>
<td>-195.82</td>
</tr>
<tr>
<td>700</td>
<td>330.56</td>
<td>141.62</td>
<td>188.94</td>
<td>-4.984</td>
<td>-193.93</td>
</tr>
<tr>
<td>800</td>
<td>338.02</td>
<td>152.19</td>
<td>185.84</td>
<td>-5.839</td>
<td>-191.68</td>
</tr>
<tr>
<td>900</td>
<td>344.63</td>
<td>162.96</td>
<td>181.67</td>
<td>-7.238</td>
<td>-188.91</td>
</tr>
<tr>
<td>1000</td>
<td>350.59</td>
<td>174.38</td>
<td>176.21</td>
<td>-8.189</td>
<td>-184.40</td>
</tr>
<tr>
<td>1100</td>
<td>356.01</td>
<td>185.11</td>
<td>170.90</td>
<td>-9.108</td>
<td>-180.01</td>
</tr>
</tbody>
</table>
Table 5.2.12. Temperature dependence of the enthalpy of polonium dioxide formation from gaseous mono-atomic elements. Sublimation enthalpy of PoO$_2$ and its vapour pressure.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta H^*_T$ (form) PoO$_2$ (kJmol$^{-1}$)</th>
<th>$\Delta H^*_T$ (form) PoO$_2$ (kJmol$^{-1}$)</th>
<th>$\Delta H_T$ (subl) PoO$_2$ (kJmol$^{-1}$)</th>
<th>log p PoO$_2$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-690.6</td>
<td>-1054.2</td>
<td>363.7</td>
<td>-53.0847</td>
</tr>
<tr>
<td>300</td>
<td>-690.5</td>
<td>-1054.1</td>
<td>363.6</td>
<td>-52.6527</td>
</tr>
<tr>
<td>400</td>
<td>-684.2</td>
<td>-1053.8</td>
<td>369.6</td>
<td>-37.9440</td>
</tr>
<tr>
<td>500</td>
<td>-685.2</td>
<td>-1053.2</td>
<td>368.0</td>
<td>-28.3177</td>
</tr>
<tr>
<td>600</td>
<td>-688.5</td>
<td>-1052.4</td>
<td>364.0</td>
<td>-21.6786</td>
</tr>
<tr>
<td>700</td>
<td>-692.6</td>
<td>-1051.1</td>
<td>358.5</td>
<td>-16.8783</td>
</tr>
<tr>
<td>800</td>
<td>-697.3</td>
<td>-1050.6</td>
<td>353.3</td>
<td>-13.3618</td>
</tr>
<tr>
<td>900</td>
<td>-699.0</td>
<td>-1049.9</td>
<td>350.9</td>
<td>-10.8769</td>
</tr>
<tr>
<td>1000</td>
<td>-702.0</td>
<td>-1049.0</td>
<td>347.0</td>
<td>- 8.9211</td>
</tr>
</tbody>
</table>

Equilibrium constants for the following reactions were calculated from entropy and enthalpy values:

Formation reaction:  
Po (cond) + O$_2$ (g) $\leftrightarrow$ PoO$_2$ (s) (5.17)

Dissociation:  
PoO$_2$ (cond) $\leftrightarrow$ Po (g) + O$_2$ (g) (5.18)

2 PoO$_2$ (cond) $\leftrightarrow$ Po$_2$ (g) + 2 O$_2$ (5.19)

Reduction with hydrogen:  
PoO$_2$ (s) + 2 H$_2$ (g) $\leftrightarrow$ Po (cond) + 2H$_2$O (g) (5.20)

Reduction with lead:  
PoO$_2$ (s) + 2 Pb (cond) $\leftrightarrow$ Po (cond) + 2PbO (s) (5.21)

Reduction with bismuth:  
3PoO$_2$ (s) + 4 Bi (cond) $\leftrightarrow$ 3Po (cond) + 2 Bi$_2$O$_3$ (s) (5.22)

The calculated equilibrium constants are shown in Table 5.2.13. The calculated values generally reflect the actually observed chemical behaviour of polonium dioxide [Gmelin, 1990]. Nevertheless, it is possible that the enthalpy of formation of solid PoO$_2$ is overestimated. The dissociative volatilisation of PoO$_2$ observed in vacuum as observed opposed to the congruent sublimation of PoO$_2$ in the presence of oxygen can not be explained by these data. However, it remains to be clarified to what extent radiolysis effects may play an additional role in the volatilisation process.

Table 5.2.13. Equilibrium constants of formation, dissociation and some redox reactions of polonium dioxide

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\text{lgK}$ Eq. (5.17)</th>
<th>$\text{lgK}$ Eq. (5.18)</th>
<th>$\text{lgK}$ Eq. (5.19)</th>
<th>$\text{lgK}$ Eq. (5.20)</th>
<th>$\text{lgK}$ Eq. (5.21)</th>
<th>$\text{lgK}$ Eq. (5.22)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>55.0186</td>
<td>-91.9491</td>
<td>-151.6368</td>
<td>25.0874</td>
<td>11.0814</td>
<td>7.8522</td>
</tr>
<tr>
<td>300</td>
<td>54.5810</td>
<td>-91.2891</td>
<td>-150.5667</td>
<td>25.0030</td>
<td>11.0490</td>
<td>7.9350</td>
</tr>
<tr>
<td>400</td>
<td>38.6900</td>
<td>-67.4778</td>
<td>-113.3430</td>
<td>19.8000</td>
<td>7.9740</td>
<td>5.7201</td>
</tr>
<tr>
<td>600</td>
<td>22.4892</td>
<td>-31.9854</td>
<td>-54.9718</td>
<td>12.0496</td>
<td>3.6396</td>
<td>2.5329</td>
</tr>
<tr>
<td>700</td>
<td>17.8969</td>
<td>-22.8200</td>
<td>-40.8111</td>
<td>9.3079</td>
<td>1.9299</td>
<td>0.2755</td>
</tr>
<tr>
<td>800</td>
<td>14.5364</td>
<td>-25.1956</td>
<td>-44.2274</td>
<td>10.1218</td>
<td>2.4498</td>
<td>0.8614</td>
</tr>
<tr>
<td>1100</td>
<td>8.4682</td>
<td>-42.9985</td>
<td>-69.0618</td>
<td>13.7639</td>
<td>5.0828</td>
<td>4.2965</td>
</tr>
</tbody>
</table>
5.2.3 Evaluation of thermochemical data for binary polonium containing systems by means of the semi-empirical Miedema model

Thermochemical data for binary metal-polonium systems have been calculated using the semi-empirical Miedema model [Boer, 1988]. The Miedema model is a semi-empirical model for the calculation of enthalpies of formation and enthalpies of mixing in solid and liquid binary metal systems. The element specific constants involved in the calculations are derived from properties of the elements and subsequently adjusted to give the best possible fit to known experimental enthalpy data. In spite of this empirical character, the physical significance of the parameters is obvious. Therefore, the classification of the model as semi-empirical is justified. Through the process of adjustment of parameters to experimental data, the model incorporates the complete knowledge of enthalpy effects in binary alloy systems.

The Miedema model is a cellular model. The principles and applications of the model are discussed in detail in [Boer, 1988]. Within the framework of the model, an alloy is thought to be built up from atomic cells of the constituent elements, each with a defined atomic volume. When cells of two different elements A and B are brought into contact to form an alloy (Figure 5.2.2), there will be discontinuities of the electron density $n_{ws}$ at the boundaries of their (Wigner-Seitz) atomic cells. To eliminate these discontinuities, a rearrangement of the electron distribution within the atomic cell is required. This involves a transfer of electrons into higher energy levels and thus leads to a positive contribution to the enthalpy of formation or mixing. This positive contribution is found to be proportional to the squared differences in cube root of the electron densities, $n_{ws}^{1/3}$, of the constituent elements in the state of a bulk metal.

Values for $n_{ws}$ for transition metals have been derived from experimental data of the bulk modulus and molar volume. For non-transition metals, a superposition of the charge densities of free atoms placed at individual lattice points was found to be an acceptable approximation for $n_{ws}$ [Boer, 1988].

Figure 5.2.2. Schematic cellular model of the formation of an alloy AB from two pure metals A and B [Boer, 1988]

A negative contribution to the enthalpies of formation or mixing, which is stabilising with respect to the constituent elements, arises from the equalisation of the chemical potential of the electronic charge, $\Phi^e$, between dissimilar atomic cells. $\Phi^e$, also called Miedema-electronegativity, was originally derived from the work functions of the pure metals and afterwards adjusted using available experimental data of enthalpies of formation. This contribution is proportional to the square of the differences of Miedema-Electronegativities of the constituent elements. Thus, for the interfacial enthalpy effect between neighbouring atomic cells we arrive at the following proportionality:

$$\Delta H_{interface} \propto -P(\Delta \Phi^e)^2 + Q(\Delta n_{ws}^{1/3})^2$$

(5.23)
where $\Delta H^{\text{interface}}$ is the enthalpy effect at the interface between dissimilar atomic cells, $P$ and $Q$ are the empirical constants for specific combinations of metals, tabulated in [Boer, 1988], $\Delta \Phi^*$ is the difference of Miedema electronegativities of the constituents and $\Delta n_{\text{ws}}$ is the difference of electron densities at the Wigner-Seitz cell boundary of the constituents.

A quantification of this relation, as discussed extensively in [Boer, 1988], involves the introduction of several other group and element specific constants and leads to the following equations for the enthalpies of formation of ordered solid alloys $A_{x_A}B_{x_B}$:

$$
\Delta H^f_{A_{x_A}B_{x_B}} (s) = x_A V_{A_{\text{alloy}}}^{2/3} f_B^{A} \left[ -P(\Delta \Phi^*)^2 + Q(\Delta n_{\text{ws}})^{1/3} - R_m \right]/ [(n_{\text{ws}} A)^{-1/3} + (n_{\text{ws}} B)^{-1/3}] + x_A \Delta H^{\text{trans}} A + x_B \Delta H^{\text{trans}} B
$$

and for the partial molar enthalpies of solution at infinite dilution in solid (liquid) mixtures of A and B:

$$
\Delta \bar{H}_{\text{solv}}^\text{A in B} (l) = 2 V_{A_{\text{alloy}}}^{2/3} \left[ -P(\Delta \Phi^*)^2 + Q(\Delta n_{\text{ws}})^{1/3} - R_{m,\text{liquid}} \right]/ [(n_{\text{ws}} A)^{-1/3} + (n_{\text{ws}} B)^{-1/3}]
$$

with:

- $\Delta H^f_{A_{x_A}B_{x_B}} (s)$: enthalpy of formation of an alloy of composition $A_{x_A}B_{x_B}$;
- $\Delta \bar{H}_{\text{solv}}^\text{A in B} (l)$: partial molar enthalpy of solution of component A in B at infinite dilution;
- $x_A$ and $x_B$: mole fraction of component A and B, respectively ($x_A + x_B = 1$);
- $V_{A_{\text{alloy}}}$: atomic volume of component A within the alloy;
- $f_B^{A}$: degree to which an atomic cell of metal A is in contact with dissimilar atomic cells of metal B on average, has been determined empirical for statistically ordered and ordered alloys [Boer, 1988];
- $P$, $Q$: empirical constants for specific combinations of metals, tabulated in [Boer, 1988];
- $\Delta \Phi^*$: difference of Miedema Electronegativities of the constituents;
- $\Delta n_{\text{ws}}$: difference of Electron densities at the Wigner-Seitz cell boundary of the constituents;
- $R_m$: hybridisation term that was introduced to account for an additional enthalpy contribution due to interaction of d- and p-orbitals in solid compounds of transition metals with non transition metals, treated as a group-specific constant within the Miedema model;
- $R_{m,\text{liquid}}$: for liquid mixtures a reduced hybridisation term has to be used: $R_{m,\text{liquid}} = 0.73R_m$;
- $\Delta H^{\text{trans}} A$, $B$: enthalpies for the transformation of elements A and B into a hypothetical metallic state (for semi- or non-metallic elements).

For a detailed discussion of the model see [Boer, 1988].
A consistent set of Miedema parameters was developed for the elements of the chalcogen group (Group 16 of the periodic table of the elements: O, S, Se, Te, Po) from the results of quantum chemical calculations as well as empirical correlations with physical properties related to electronegativity and electron density [Neuhausen, 2003]. The values of these parameters are listed in Table 5.2.14. For details of the derivation of parameters we refer to the original literature [Neuhausen, 2003].

### Table 5.2.14. Miedema parameters for the elements of the chalcogen group

<table>
<thead>
<tr>
<th>Element</th>
<th>n_{ws}^{1/3} [d.u.]</th>
<th>Φ* [V]</th>
<th>V^{2/3} [cm^2 mol^{-2/3}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1.70</td>
<td>6.97</td>
<td>2.656</td>
</tr>
<tr>
<td>S</td>
<td>1.46</td>
<td>5.60</td>
<td>4.376</td>
</tr>
<tr>
<td>Se</td>
<td>1.40</td>
<td>5.17</td>
<td>5.172</td>
</tr>
<tr>
<td>Te</td>
<td>1.31</td>
<td>4.72</td>
<td>6.439</td>
</tr>
<tr>
<td>Po</td>
<td>1.15</td>
<td>4.44</td>
<td>7.043</td>
</tr>
</tbody>
</table>

Hybridisation term R for the chalcogen group: 2.45 V

Valence factor a for the chalcogen group: 0.04

Using this parameter set, thermochemical properties such as enthalpies of formation of solid metal chalcogenides, partial molar enthalpies of solution of chalcogens in liquid and solid metals, partial molar enthalpies of evaporation of the chalcogens from liquid metal solution into the monoatomic gaseous state, partial molar enthalpies of adsorption of chalcogenides on metal surfaces at zero coverage and partial molar enthalpies of segregation of the chalcogens in trace amounts within solid metal matrices have been calculated. These properties are compared with available experimental data and discussed with an emphasis on the periodic behaviour of the elements. Systematic errors of the model for specific element combinations are discussed as well. As an example, Figure 5.2.3 shows a comparison of calculated formation enthalpies for metal sulphides (bars) with the corresponding literature data (squares) [Mills, 1974]. Shaded bars correspond to metal-sulphur combinations, where a systematic underestimation of stability is known for the Miedema model.

**Figure 5.2.3.** Calculated (bars) and tabulated (squares) enthalpies of formation for one mole of sulphides M_{0.5}S_{0.5} vs. atomic number of the metal M

*White bars indicate combinations of a transition element with sulphur, whereas combinations of sulphur with main group elements, where Brillouin zone effects lead to an underestimation of stability, are symbolised by shaded bars.*
The model calculations show that a semi-quantitative description of the thermochemical properties of the chalcogens using the semi-empirical Miedema approach is possible. General trends in the formation enthalpies of metal chalcogenides throughout the periodic table are represented reasonably well by the results of calculations. It should be pointed out that the computed enthalpy values should not be considered as highly precise data. However, periodic trends and relative stabilities of series of compounds are reproduced well by the calculations Therefore, the calculated properties can serve as a basis for the prediction of the chemical interactions for metal-chalcogen combinations that have not been studied experimentally so far, i.e. especially for metal polonium combinations. Figure 5.2.4 shows a summary of calculated formation enthalpies of metal polonides of composition $M_{0.5}Po_{0.5}$ and the experimentally known qualitative facts about those metal polonium systems. In general, the agreement is satisfactory. For metal-polonium combinations were compound formation is observed, negative enthalpies of formation are calculated, whereas positive values are calculated for systems where no reaction is observed.

Enthalpy values for polonium-containing systems are compiled in Tables 5.2.15-5.2.17.

5.2.4 Analysis of thermochemical relations of iodine within a liquid LBE spallation target

For an assessment of the release properties of the halogens within a liquid LBE target, temperature dependant equilibrium constants for the formation reactions of halogen-containing species in the heterogeneous systems $\text{Pb/Bi/H/O/X (X = halogen)}$ were calculated by Eichler, et al. [Eichler, 2003] using tabulated thermodynamic data [Barin, 1995]. Based on these evaluations no predominant pathway for the formation of gaseous iodine compounds can be found.

Because of the small concentrations and presumably low thermodynamic activity coefficients for non ideal behaviour an extensive release of iodine seems unlikely even at the given operating temperatures. Volatile iodine-containing species that could be present in the gaseous phase at very low concentrations are expected to react with basic oxides or hydroxides of nuclear reaction products, thus lowering the iodine gas phase concentration even more.

A basic absorber material (CaO, Ca(OH)$_2$) located in the gas plenum has promise to preclude the presence of small amounts of gaseous iodine species. In addition, this absorber would serve for the fixation of iodine produced within the gas phase by decay of Xe isotopes.
Figure 5.2.4. Experimental information and Miedema predictions of the stability of binary polonides throughout the periodic table of the elements

Each box corresponds to the binary system of the specified element with polonium. The atomic number of the element is given in brackets. The boxes are shaded as follows: white boxes = binary system not investigated; horizontally hatched boxes = no reaction is observed between the respective element and polonium; vertically hatched boxes = reaction is observed, but the product is not well characterised; cross hatched boxes = contradictory evidence from different literature; diagonally hatched boxes = reaction is observed, reaction product characterised by x-ray diffraction or at least melting or decomposition temperature has been determined. Values for the enthalpies of formation of solid compounds of composition $M_{0.5}Po_{0.5}$ calculated using the Miedema model are given for each combination. The box for La(57) can be considered representative for the complete lanthanide series.
Table 5.2.15. Calculated enthalpies of formation ($\Delta H_f^{\text{calc}}$) of solid binary polonides obtained using Miedema parameters derived in [Neuhausen, 2003] (Table 5.2.14)

All other Miedema parameters have been taken from [Boer, 1988]. For comparison, the few available literature data and values calculated by other methods within [Neuhausen, 2003] have been included ($\Delta H_f^{\text{Lit}}$).

<table>
<thead>
<tr>
<th>Partner element</th>
<th>Composition $\text{M}_{1-x}\text{Po}_x$</th>
<th>$\Delta H_f^{\text{calc}}$ [kJmol$^{-1}$]</th>
<th>$\Delta H_f^{\text{Lit}}$ [kJmol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac</td>
<td>0.3333</td>
<td>-114.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-135.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-125.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-109.6</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.3333</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.3333</td>
<td>12.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>13.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>Am</td>
<td>0.3333</td>
<td>-99.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-113.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-101.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-88.0</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.3333</td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>20.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>17.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>15.2</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>0.3333</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>12.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.3333</td>
<td>82.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>70.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>57.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>47.4</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.3333</td>
<td>-115.0</td>
<td>-153$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-161.5$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-167.8$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-137.7$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-137.6$^e$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-149.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-143.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-129.1</td>
</tr>
<tr>
<td>Be</td>
<td>0.3333</td>
<td>51.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>45.7</td>
<td>-28.6$^f$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>37.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>31.1</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>0.3333</td>
<td>-2.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-2.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-2.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-2.3</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2.15. Calculated enthalpies of formation ($\Delta H^f_{\text{calc}}$) of solid binary polonides obtained using Miedema parameters derived in [Neuhausen, 2003] (Table 5.2.14) (cont.).

All other Miedema parameters have been taken from [Boer, 1988]. For comparison, the few available literature data and values calculated by other methods within [Neuhausen, 2003] have been included ($\Delta H^f_{\text{lit}}$).

<table>
<thead>
<tr>
<th>Partner element</th>
<th>Composition $M_{1-x}Po_x$</th>
<th>$\Delta H^f_{\text{calc}}$ [kJmol$^{-1}$]</th>
<th>$\Delta H^f_{\text{lit}}$ [kJmol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bk</td>
<td>0.3333</td>
<td>-100.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-112.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-100.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-86.3</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.3333</td>
<td>127.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>96.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>77.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>64.2</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.3333</td>
<td>-103.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-123.3</td>
<td>-128$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-140.4$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-132.1$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-135.9$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-117.3$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-121.3$^b$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-112.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-98.7</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.3333</td>
<td>-2.0</td>
<td>-1.8$^b$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-2.2</td>
<td>-29.2$^c$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-1.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-1.7</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>0.3333</td>
<td>-108.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-129.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-119.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-105.0</td>
<td></td>
</tr>
<tr>
<td>Cf</td>
<td>0.3333</td>
<td>96.9 (Cf(II))</td>
<td>-99.9(Cf(III))</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-119.4 (Cf(II))</td>
<td>-111.2 (Cf(III))</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-111.6 (Cf(II))</td>
<td>-98.9 (Cf(III))</td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-98.6 (Cf(II))</td>
<td>-85.3 (Cf(III))</td>
</tr>
<tr>
<td>Cm</td>
<td>0.3333</td>
<td>-99.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-113.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-101.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-88.3</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.3333</td>
<td>15.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>14.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>11.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.3333</td>
<td>20.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>16.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>13.8</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2.15. Calculated enthalpies of formation ($\Delta H^f_{\text{calc}}$) of solid binary polonides obtained using Miedema parameters derived in [Neuhausen, 2003] (Table 5.2.14) (cont.)

All other Miedema parameters have been taken from [Boer, 1988]. For comparison, the few available literature data and values calculated by other methods within [Neuhausen, 2003] have been included ($\Delta H^f_{\text{lit}}$).

<table>
<thead>
<tr>
<th>Partner element</th>
<th>Composition $M_{1-x}Po_x$</th>
<th>$\Delta H^f_{\text{calc}}$ [kJmol$^{-1}$]</th>
<th>$\Delta H^f_{\text{lit}}$ [kJmol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>0.3333</td>
<td>-55.8</td>
<td>-114$^a$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-79.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-80.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-74.5</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.3333</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>0.3333</td>
<td>-104.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-121.1</td>
<td>-115.2$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-154.0$^g$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-109.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-95.5</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>0.3333</td>
<td>-103.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-118.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-107.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-93.1</td>
<td></td>
</tr>
<tr>
<td>Es</td>
<td>0.3333</td>
<td>-116.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-143.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-134.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-119.3</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>0.3333</td>
<td>-103.5 (Eu(II))</td>
<td>-147.8$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-42.3 (Eu(III))</td>
<td>-152.7$^d$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-126.6 (Eu(II))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-76.3 (Eu(III))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-117.5 (Eu(II))</td>
<td>-111$^b$</td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-103.4 (Eu(II))</td>
<td>-67.1 (Eu(III))</td>
</tr>
<tr>
<td>Fe</td>
<td>0.3333</td>
<td>28.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>27.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>22.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>19.2</td>
<td></td>
</tr>
<tr>
<td>Fm</td>
<td>0.3333</td>
<td>-111.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-132.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-121.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-106.1</td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>0.3333</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>0.3333</td>
<td>-106.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-124.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-113.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-98.8</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2.15. Calculated enthalpies of formation ($\Delta H_f^{calc}$) of solid binary polonides obtained using Miedema parameters derived in [Neuhausen, 2003] (Table 5.2.14) (cont.)

All other Miedema parameters have been taken from [Boer, 1988]. For comparison, the few available literature data and values calculated by other methods within [Neuhausen, 2003] have been included ($\Delta H_f^{Lit}$).

<table>
<thead>
<tr>
<th>Partner element</th>
<th>Composition $M_{1-x}Po_x$</th>
<th>$\Delta H_f^{calc}$ [kJmol$^{-1}$]</th>
<th>$\Delta H_f^{Lit}$ [kJmol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.3333</td>
<td>28.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>24.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>20.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>17.1</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.3333</td>
<td>74.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>56.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>44.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>37.3</td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>0.3333</td>
<td>-77.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-84.4</td>
<td>-2.8$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-3.4$^c$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-74.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-63.7</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.3333</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>0.6</td>
<td>-10.5$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.7$^c$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Ho</td>
<td>0.3333</td>
<td>-103.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-119.6</td>
<td>-116.8$^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-141.4$^g$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-132$^h$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-108.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-94.1</td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>0.3333</td>
<td>-7.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-8.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-7.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-6.9</td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>0.3333</td>
<td>21.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>22.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>19.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>16.2</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.3333</td>
<td>-53.4</td>
<td>-123$^i$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-70.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-67.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-60.1</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>0.3333</td>
<td>-109.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-132.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-122.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-108.1</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>0.3333</td>
<td>-52.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-50.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-42.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-35.8</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2.15. Calculated enthalpies of formation ($\Delta H^f_{\text{calc}}$) of solid binary polonides obtained using Miedema parameters derived in [Neuhausen, 2003] (Table 5.2.14) (cont.)

All other Miedema parameters have been taken from [Boer, 1988]. For comparison, the few available literature data and values calculated by other methods within [Neuhausen, 2003] have been included ($\Delta H^f_{\text{Lit}}$).

<table>
<thead>
<tr>
<th>Partner element</th>
<th>Composition $M_{1-x}$Po$_x$</th>
<th>$\Delta H^f_{\text{calc}}$ [kJmol$^{-1}$]</th>
<th>$\Delta H^f_{\text{Lit}}$ [kJmol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lu</td>
<td>0.3333</td>
<td>-103.0</td>
<td>-72.6$^b$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-116.8</td>
<td>-8.8$^c$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-105.0</td>
<td>-13.6$^a$</td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-90.9</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.3333</td>
<td>-25.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-27.5</td>
<td>-27$^a$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-23.9</td>
<td>-56.9$^a$</td>
</tr>
<tr>
<td>Mn</td>
<td>0.3333</td>
<td>-13.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-13.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-11.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-9.3</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.3333</td>
<td>37.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>38.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>32.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>27.7</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.3333</td>
<td>130.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>87.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>68.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>57.5</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.3333</td>
<td>-47.7</td>
<td>-116$^a$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-54.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-48.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-41.3</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>0.3333</td>
<td>-11.7</td>
<td>40.9$^a$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-12.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-10.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-8.9</td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>0.3333</td>
<td>-107.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-126.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-116.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-101.5</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.3333</td>
<td>10.7</td>
<td>-23.6$^a$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>10.2</td>
<td>6.3$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-23.4$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-19.2$^b$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td>Np</td>
<td>0.3333</td>
<td>-59.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-62.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-53.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-45.9</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0.3333</td>
<td>-79.9</td>
<td>-84.2 (8.4)$^d$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-72.2</td>
<td>-84.4$^e$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-58.9</td>
<td>-83.7$^f$</td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-49.0</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2.15. Calculated enthalpies of formation ($\Delta H_{\text{calc}}^{f}$) of solid binary polonides obtained using Miedema parameters derived in [Neuhausen, 2003] (Table 5.2.14) (cont.)

All other Miedema parameters have been taken from [Boer, 1988]. For comparison, the few available literature data and values calculated by other methods within [Neuhausen, 2003] have been included ($\Delta H_{\text{lit}}^{f}$).

<table>
<thead>
<tr>
<th>Partner element</th>
<th>Composition $M_{1-x}Pox$</th>
<th>$\Delta H_{\text{calc}}^{f}$ [kJmol$^{-1}$]</th>
<th>$\Delta H_{\text{lit}}^{f}$ [kJmol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>0.3333</td>
<td>40.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>41.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>35.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>29.8</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.3333</td>
<td>41.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>39.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>33.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>28.2</td>
<td></td>
</tr>
<tr>
<td>Pa</td>
<td>0.3333</td>
<td>-118.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-131.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-116.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-100.4</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.3333</td>
<td>-3.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-3.7</td>
<td>-29.4$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-18.2$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-33.9$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-28.3$^b$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-3.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-3.0</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>0.3333</td>
<td>-29.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-30.7</td>
<td>-29.4$^d$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-26.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-22.3</td>
<td></td>
</tr>
<tr>
<td>Pm</td>
<td>0.3333</td>
<td>-107.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-125.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-115.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-100.6</td>
<td></td>
</tr>
<tr>
<td>Pr</td>
<td>0.3333</td>
<td>-107.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-127.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-116.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-102.1</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>0.3333</td>
<td>-6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-6.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-5.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-4.6</td>
<td>-23.3$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-27.4$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-13.8$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-10.5$^i$</td>
</tr>
<tr>
<td>Pu</td>
<td>0.3333</td>
<td>-84.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-89.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-77.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-65.9</td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>0.3333</td>
<td>-55.0</td>
<td>-112$^a$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-75.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-74.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-67.4</td>
<td></td>
</tr>
<tr>
<td>Re</td>
<td>0.3333</td>
<td>52.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>53.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>46.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>39.1</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2.15. Calculated enthalpies of formation ($\Delta H^f_{\text{calc}}$) of solid binary polonides obtained using Miedema parameters derived in [Neuhausen, 2003] (Table 5.2.14) (cont.)

All other Miedema parameters have been taken from [Boer, 1988]. For comparison, the few available literature data and values calculated by other methods within [Neuhausen, 2003] have been included ($\Delta H^f_{\text{Lit}}$).

<table>
<thead>
<tr>
<th>Partner element</th>
<th>Composition $M_{1-x}Po_x$</th>
<th>$\Delta H^f_{\text{calc}}$ [kJmol$^{-1}$]</th>
<th>$\Delta H^f_{\text{Lit}}$ [kJmol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>0.3333</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>0.3333</td>
<td>31.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>32.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>27.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>23.0</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.3333</td>
<td>-11.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-12.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-10.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-8.9</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>0.3333</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Sc</td>
<td>0.3333</td>
<td>-97.1</td>
<td>-81.1$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-92.5$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-76.7$^g$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-124$^h$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-105.5</td>
<td>-92.5$^c$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-92.8</td>
<td>-76.7$^g$</td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-92.6</td>
<td>-124$^h$</td>
</tr>
<tr>
<td>Se</td>
<td>0.3333</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.3333</td>
<td>51.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>45.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>38.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>32.0</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>0.3333</td>
<td>-106.4</td>
<td>-134a</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-124.4</td>
<td>-155.6b</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-113.6</td>
<td>-141.6c</td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-99.2</td>
<td>-156.2g</td>
</tr>
<tr>
<td>Sn</td>
<td>0.3333</td>
<td>-0.2</td>
<td>-134a</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-0.3</td>
<td>-155.6b</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-0.2</td>
<td>-141.6c</td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-0.2</td>
<td>-156.2g</td>
</tr>
<tr>
<td>Sr</td>
<td>0.3333</td>
<td>-106.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-135.1</td>
<td>-134a</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-128.2</td>
<td>-155.6b</td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-114.0</td>
<td>-141.6c</td>
</tr>
<tr>
<td>Ta</td>
<td>0.3333</td>
<td>-14.7</td>
<td>76.4$^c$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-15.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-13.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-11.2</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2.15. Calculated enthalpies of formation ($\Delta H_{\text{calc}}^f$) of solid binary polonides obtained using Miedema parameters derived in [Neuhausen, 2003] (Table 5.2.14) (*cont.*)

All other Miedema parameters have been taken from [Boer, 1988]. For comparison, the few available literature data and values calculated by other methods within [Neuhausen, 2003] have been included ($\Delta H_{\text{lit}}^f$)

<table>
<thead>
<tr>
<th>Partner element</th>
<th>Composition $M_{1-x}Po_x$</th>
<th>$\Delta H_{\text{calc}}^f$ [kJmol$^{-1}$]</th>
<th>$\Delta H_{\text{lit}}^f$ [kJmol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb</td>
<td>0.3333 MA</td>
<td>-105.1</td>
<td>-112.7$^b$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-121.9</td>
<td>-108.0$^c$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-110.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-96.5</td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>0.3333 MA</td>
<td>29.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>30.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>25.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>0.3333 MA</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>0.3333 MA</td>
<td>-108.7</td>
<td>-29.6$^b$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-128.3</td>
<td>-29.2$^c$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-118.2</td>
<td>-47.5$^d$</td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-103.7</td>
<td>-45.5$^b$</td>
</tr>
<tr>
<td>Ti</td>
<td>0.3333 MA</td>
<td>-51.4</td>
<td>-24.8$^d$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-52.7</td>
<td>-29.6$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-29.2$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-47.5$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-45.5$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-24.8$^d$</td>
</tr>
<tr>
<td>Tm</td>
<td>0.3333 MA</td>
<td>-103.4</td>
<td>-120.4$^b$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-117.9</td>
<td>-144.8g</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-106.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-92.1</td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>0.3333 MA</td>
<td>-68.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-72.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-63.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-54.2</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.3333 MA</td>
<td>-7.1</td>
<td>43.1$c$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-7.1</td>
<td>43.1$c$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-5.0</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>0.3333 MA</td>
<td>51.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>52.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>45.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>38.5</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>0.3333 MA</td>
<td>-106.3</td>
<td>-100.4$b$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-124.1</td>
<td>-102.3$c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-38.8$^d$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-113.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-98.8</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2.15. Calculated enthalpies of formation ($\Delta H^f_{\text{calc}}$) of solid binary polonides obtained using Miedema parameters derived in [Neuhausen, 2003] (Table 5.2.14) (cont.)

All other Miedema parameters have been taken from [Boer, 1988]. For comparison, the few available literature data and values calculated by other methods within [Neuhausen, 2003] have been included ($\Delta H^f_{\text{Lit}}$).

<table>
<thead>
<tr>
<th>Partner element</th>
<th>Composition $M_{1-x}Po_x$</th>
<th>$\Delta H^f_{\text{calc}}$ [kJmol$^{-1}$]</th>
<th>$\Delta H^f_{\text{Lit}}$ [kJmol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb</td>
<td>0.3333</td>
<td>-101.6 (Yb(II))</td>
<td>-114.0$^b$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-119.8 (Yb(II))</td>
<td>-122.2$^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-97.0 (Yb(III))</td>
<td>-125$^b$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-108.9 (Yb(II))</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-89.3 (Yb(III))</td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>0.6667</td>
<td>-94.9 (Yb(II))</td>
<td>-114.0$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-78.0 (Yb(III))</td>
<td>-122.2$^f$</td>
</tr>
<tr>
<td>Zn</td>
<td>0.3333</td>
<td>4.0</td>
<td>-24.1$^e$</td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>0.3333</td>
<td>-94.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5000</td>
<td>-102.5</td>
<td>-27.6$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-38.1$^e$</td>
</tr>
<tr>
<td></td>
<td>0.6000</td>
<td>-90.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6667</td>
<td>-77.7</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ [Krestov, 1962].

$^b$ LMTO calculations [Neuhausen, 2003].

$^c$ PP-PW calculations [Neuhausen, 2003].

$^d$ [Brewer, 1953].

$^e$ [Latimer, 1952].

$^f$ [Zhdanov, 1985].

$^g$ Calculated from Kapustinskii lattice energies, ionisation energies and sublimation enthalpies [Neuhausen, 2003].

$^h$ Estimated from linear correlations with lnA in homologous series MQ (Q = S, Se, Te) [Neuhausen, 2003].

$^i$ Estimated from linear correlations with covalent radius of the chalcogen in homologous series MQ (Q = S, Se, Te) [Neuhausen, 2003].

$^k$ Estimated from linear correlations with ionic radius of the chalcogen in homologous series MQ (Q = S, Se, Te) [Neuhausen, 2003].
Table 5.2.16. Calculated values for the partial molar enthalpy of solution of liquid polonium in liquid elements B at infinite dilution and calculated partial molar enthalpies of evaporation of polonium into the monoatomic state from liquid metal solutions [Neuhausen, 2003]

<table>
<thead>
<tr>
<th>Symbol of element B</th>
<th>Atomic number Z</th>
<th>$\Delta H^{\text{mol}}_{\text{Poin B(l)}} (\text{calc.})$ [kJmol$^{-1}$]</th>
<th>$\Delta H^\text{vap}_{\text{Poin B(l)}} (\text{calc.})$ [kJmol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac</td>
<td>89</td>
<td>-322.4</td>
<td>511.3</td>
</tr>
<tr>
<td>Ag</td>
<td>47</td>
<td>15.0</td>
<td>173.9</td>
</tr>
<tr>
<td>Al</td>
<td>13</td>
<td>46.5</td>
<td>142.4</td>
</tr>
<tr>
<td>Am</td>
<td>95</td>
<td>-279.3</td>
<td>468.2</td>
</tr>
<tr>
<td>As</td>
<td>33</td>
<td>63.0</td>
<td>125.9</td>
</tr>
<tr>
<td>Au</td>
<td>79</td>
<td>69.3</td>
<td>119.6</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>268.1</td>
<td>-79.2</td>
</tr>
<tr>
<td>Ba</td>
<td>56</td>
<td>-335.5</td>
<td>524.4</td>
</tr>
<tr>
<td>Be</td>
<td>4</td>
<td>218.1</td>
<td>-29.2</td>
</tr>
<tr>
<td>Bi</td>
<td>83</td>
<td>-7.3</td>
<td>196.2</td>
</tr>
<tr>
<td>Bk</td>
<td>97</td>
<td>-282.8</td>
<td>471.7</td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>36.5</td>
<td>152.4</td>
</tr>
<tr>
<td>Ca</td>
<td>20</td>
<td>-309.6</td>
<td>498.5</td>
</tr>
<tr>
<td>Cd</td>
<td>48</td>
<td>-7.0</td>
<td>195.9</td>
</tr>
<tr>
<td>Ce</td>
<td>58</td>
<td>-301.8</td>
<td>490.7</td>
</tr>
<tr>
<td>CHII</td>
<td>98</td>
<td>-285.8</td>
<td>474.7</td>
</tr>
<tr>
<td>CHIII</td>
<td>98</td>
<td>-283.3</td>
<td>472.2</td>
</tr>
<tr>
<td>Cm</td>
<td>96</td>
<td>-275.6</td>
<td>464.5</td>
</tr>
<tr>
<td>Co</td>
<td>27</td>
<td>136.3</td>
<td>52.6</td>
</tr>
<tr>
<td>Cr</td>
<td>24</td>
<td>158.4</td>
<td>30.5</td>
</tr>
<tr>
<td>Cs</td>
<td>55</td>
<td>-174.3</td>
<td>363.2</td>
</tr>
<tr>
<td>Cu</td>
<td>29</td>
<td>47.8</td>
<td>141.1</td>
</tr>
<tr>
<td>Dy</td>
<td>66</td>
<td>-293.8</td>
<td>482.7</td>
</tr>
<tr>
<td>Er</td>
<td>68</td>
<td>-290.6</td>
<td>479.5</td>
</tr>
<tr>
<td>Es</td>
<td>99</td>
<td>-342.5</td>
<td>531.4</td>
</tr>
<tr>
<td>EuII</td>
<td>63</td>
<td>-308.3</td>
<td>497.2</td>
</tr>
<tr>
<td>EuIII</td>
<td>63</td>
<td>-296.7</td>
<td>485.6</td>
</tr>
<tr>
<td>Fe</td>
<td>26</td>
<td>188.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Fm</td>
<td>100</td>
<td>-331.1</td>
<td>520.0</td>
</tr>
<tr>
<td>Ga</td>
<td>31</td>
<td>11.7</td>
<td>177.2</td>
</tr>
<tr>
<td>Gd</td>
<td>64</td>
<td>-296.7</td>
<td>485.6</td>
</tr>
<tr>
<td>Ge</td>
<td>32</td>
<td>41.7</td>
<td>147.2</td>
</tr>
<tr>
<td>Hf</td>
<td>72</td>
<td>-190.1</td>
<td>379.0</td>
</tr>
<tr>
<td>Hg</td>
<td>80</td>
<td>1.7</td>
<td>187.2</td>
</tr>
<tr>
<td>Ho</td>
<td>67</td>
<td>-291.0</td>
<td>479.9</td>
</tr>
<tr>
<td>In</td>
<td>49</td>
<td>-25.8</td>
<td>214.7</td>
</tr>
<tr>
<td>Ir</td>
<td>77</td>
<td>155.7</td>
<td>33.2</td>
</tr>
<tr>
<td>K</td>
<td>19</td>
<td>-167.1</td>
<td>356.0</td>
</tr>
<tr>
<td>La</td>
<td>57</td>
<td>-304.1</td>
<td>493.0</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>-192.1</td>
<td>381.0</td>
</tr>
<tr>
<td>Lu</td>
<td>71</td>
<td>-290.0</td>
<td>478.9</td>
</tr>
<tr>
<td>Mg</td>
<td>12</td>
<td>-89.0</td>
<td>277.9</td>
</tr>
<tr>
<td>Mn</td>
<td>25</td>
<td>23.4</td>
<td>165.5</td>
</tr>
<tr>
<td>Mo</td>
<td>42</td>
<td>214.1</td>
<td>-25.2</td>
</tr>
</tbody>
</table>
Table 5.2.16. Calculated values for the partial molar enthalpy of solution of liquid polonium in liquid elements B at infinite dilution and calculated partial molar enthalpies of evaporation of polonium into the monoatomic state from liquid metal solutions [Neuhausen, 2003] (cont.)

<table>
<thead>
<tr>
<th>Symbol of element B</th>
<th>Atomic number Z</th>
<th>( \Delta H^\text{sol} \text{Poin B(3)} \text{(calc.)} ) [kJmol(^{-1})]</th>
<th>( \Delta H^\text{vap} \text{Poin B(3)} \text{(calc.)} ) [kJmol(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>11</td>
<td>-155.2</td>
<td>344.1</td>
</tr>
<tr>
<td>Nb</td>
<td>41</td>
<td>37.8</td>
<td>151.1</td>
</tr>
<tr>
<td>Nd</td>
<td>60</td>
<td>-299.4</td>
<td>488.3</td>
</tr>
<tr>
<td>Ni</td>
<td>28</td>
<td>119.1</td>
<td>69.8</td>
</tr>
<tr>
<td>Np</td>
<td>93</td>
<td>-131.4</td>
<td>320.3</td>
</tr>
<tr>
<td>Os</td>
<td>76</td>
<td>224.9</td>
<td>-36.0</td>
</tr>
<tr>
<td>P</td>
<td>15</td>
<td>109.5</td>
<td>79.4</td>
</tr>
<tr>
<td>Pa</td>
<td>91</td>
<td>-327.7</td>
<td>516.6</td>
</tr>
<tr>
<td>Pb</td>
<td>82</td>
<td>-10.2</td>
<td>199.1</td>
</tr>
<tr>
<td>Pd</td>
<td>46</td>
<td>-30.3</td>
<td>219.2</td>
</tr>
<tr>
<td>Pm</td>
<td>61</td>
<td>-299.5</td>
<td>488.4</td>
</tr>
<tr>
<td>Po</td>
<td>84</td>
<td>0</td>
<td>188.9</td>
</tr>
<tr>
<td>Pr</td>
<td>59</td>
<td>-299.4</td>
<td>488.3</td>
</tr>
<tr>
<td>Pt</td>
<td>78</td>
<td>55.3</td>
<td>133.6</td>
</tr>
<tr>
<td>Pu</td>
<td>94</td>
<td>-221.3</td>
<td>410.2</td>
</tr>
<tr>
<td>Rb</td>
<td>37</td>
<td>-171.7</td>
<td>360.6</td>
</tr>
<tr>
<td>Re</td>
<td>75</td>
<td>267.9</td>
<td>-79.0</td>
</tr>
<tr>
<td>Rh</td>
<td>45</td>
<td>91.6</td>
<td>97.3</td>
</tr>
<tr>
<td>Ru</td>
<td>44</td>
<td>193.3</td>
<td>-4.4</td>
</tr>
<tr>
<td>S</td>
<td>16</td>
<td>-41.0</td>
<td>229.9</td>
</tr>
<tr>
<td>Sb</td>
<td>51</td>
<td>10.2</td>
<td>178.7</td>
</tr>
<tr>
<td>Sc</td>
<td>21</td>
<td>-278.6</td>
<td>467.5</td>
</tr>
<tr>
<td>Se</td>
<td>34</td>
<td>5.1</td>
<td>183.8</td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>105.6</td>
<td>83.3</td>
</tr>
<tr>
<td>Sm</td>
<td>62</td>
<td>-296.7</td>
<td>485.6</td>
</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>-0.7</td>
<td>189.6</td>
</tr>
<tr>
<td>Sr</td>
<td>38</td>
<td>-315.6</td>
<td>504.5</td>
</tr>
<tr>
<td>Ta</td>
<td>73</td>
<td>26.8</td>
<td>162.1</td>
</tr>
<tr>
<td>Tb</td>
<td>65</td>
<td>-293.8</td>
<td>482.7</td>
</tr>
<tr>
<td>Tc</td>
<td>43</td>
<td>185.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Te</td>
<td>52</td>
<td>14.9</td>
<td>174.0</td>
</tr>
<tr>
<td>Th</td>
<td>90</td>
<td>-302.7</td>
<td>491.6</td>
</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>-106.4</td>
<td>295.3</td>
</tr>
<tr>
<td>Tl</td>
<td>81</td>
<td>-24.8</td>
<td>213.7</td>
</tr>
<tr>
<td>Tm</td>
<td>69</td>
<td>-290.6</td>
<td>479.5</td>
</tr>
<tr>
<td>U</td>
<td>92</td>
<td>-159.1</td>
<td>348.0</td>
</tr>
<tr>
<td>V</td>
<td>23</td>
<td>51.2</td>
<td>137.7</td>
</tr>
<tr>
<td>W</td>
<td>74</td>
<td>262.4</td>
<td>-73.5</td>
</tr>
<tr>
<td>Y</td>
<td>39</td>
<td>-296.7</td>
<td>485.6</td>
</tr>
<tr>
<td>YbII</td>
<td>70</td>
<td>-305.5</td>
<td>494.4</td>
</tr>
<tr>
<td>YbIII</td>
<td>70</td>
<td>-290.6</td>
<td>479.5</td>
</tr>
<tr>
<td>Zn</td>
<td>30</td>
<td>14.7</td>
<td>174.2</td>
</tr>
<tr>
<td>Zr</td>
<td>40</td>
<td>-244.4</td>
<td>433.3</td>
</tr>
</tbody>
</table>
Table 5.2.17. Calculated values for the partial molar enthalpy of solution of polonium in solid elements B at infinite dilution, mechanism of polonium adsorption on/in solid surfaces of element B, see [Neuhausen, 2003], partial molar enthalpies of adsorption of polonium in/on solid surfaces of B at zero coverage, partial molar net enthalpies of adsorption of polonium in/on solid surfaces of B at zero coverage and partial molar enthalpies of segregation of polonium in a solid matrix of B

<table>
<thead>
<tr>
<th>Element B</th>
<th>Atomic number Z</th>
<th>( \Delta H_{\text{ads}} ) Po in B (s) (calc.) [kJmol(^{-1})]</th>
<th>Adsorption mechanism</th>
<th>( \Delta H_{\text{ads}} ) Po in/on B (calc.) [kJmol(^{-1})]</th>
<th>( \Delta H_{\text{ads,net}} ) Po in/on B (calc.) [kJmol(^{-1})]</th>
<th>( \Delta H_{\text{seg}} ) Po (calc.) [kJmol(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac 89</td>
<td>-369.8</td>
<td>In</td>
<td>-540.7</td>
<td>-351.8</td>
<td>18.1</td>
<td></td>
</tr>
<tr>
<td>Ag 47</td>
<td>4.2</td>
<td>In</td>
<td>-212.8</td>
<td>-23.9</td>
<td>-28.1</td>
<td></td>
</tr>
<tr>
<td>Al 13</td>
<td>46.5</td>
<td>In (on)</td>
<td>-167.8 (-227.8)</td>
<td>21.1 (-38.9)</td>
<td>-25.4 (-85.4)</td>
<td></td>
</tr>
<tr>
<td>Am 95</td>
<td>-330.1</td>
<td>In</td>
<td>-509.6</td>
<td>-320.7</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>As 33</td>
<td>63.0</td>
<td>On</td>
<td>-221.3</td>
<td>-32.4</td>
<td>-95.4</td>
<td></td>
</tr>
<tr>
<td>Au 79</td>
<td>47.0</td>
<td>In (on)</td>
<td>-175.8 (-254.6)</td>
<td>13.1 (-65.7)</td>
<td>-33.9 (-112.7)</td>
<td></td>
</tr>
<tr>
<td>B 5</td>
<td>268.1</td>
<td>On</td>
<td>-303.2</td>
<td>-114.3</td>
<td>-382.3</td>
<td></td>
</tr>
<tr>
<td>Be 4</td>
<td>-361.3</td>
<td>In</td>
<td>-524.2</td>
<td>-335.3</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>Be 4</td>
<td>218.1</td>
<td>On</td>
<td>-243.9</td>
<td>-55</td>
<td>-273</td>
<td></td>
</tr>
<tr>
<td>Bi 83</td>
<td>-7.3</td>
<td>In</td>
<td>-203.6</td>
<td>-14.7</td>
<td>-7.3</td>
<td></td>
</tr>
<tr>
<td>Bk 97</td>
<td>-333.6</td>
<td>In</td>
<td>-511.4</td>
<td>-322.5</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>C 6</td>
<td>36.5</td>
<td>In</td>
<td>-375.2</td>
<td>-186.3</td>
<td>-222.8</td>
<td></td>
</tr>
<tr>
<td>Ca 20</td>
<td>-331.5</td>
<td>In</td>
<td>-501.6</td>
<td>-312.7</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>Cd 48</td>
<td>-7.0</td>
<td>In</td>
<td>-206.7</td>
<td>-17.8</td>
<td>-10.8</td>
<td></td>
</tr>
<tr>
<td>Ce 58</td>
<td>-351.3</td>
<td>In</td>
<td>-520.4</td>
<td>-331.5</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td>CfII 98</td>
<td>-308.4</td>
<td>In</td>
<td>-503.6</td>
<td>-314.7</td>
<td>19.2</td>
<td></td>
</tr>
<tr>
<td>CfIII 98</td>
<td>-333.9</td>
<td>In</td>
<td>-486.5</td>
<td>-297.6</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td>Cr 24</td>
<td>58.6</td>
<td>On (in)</td>
<td>-318.5 (-187.4)</td>
<td>-129.6 (1.5)</td>
<td>-188.2 (-57.0)</td>
<td></td>
</tr>
<tr>
<td>Cs 55</td>
<td>79.6</td>
<td>On</td>
<td>-337.5</td>
<td>-148.6</td>
<td>-228.2</td>
<td></td>
</tr>
<tr>
<td>Cu 29</td>
<td>-174.3</td>
<td>In</td>
<td>-347.8</td>
<td>-158.9</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>Dy 66</td>
<td>25.5</td>
<td>In</td>
<td>-204.7</td>
<td>-15.8</td>
<td>-41.3</td>
<td></td>
</tr>
<tr>
<td>Er 68</td>
<td>-343.8</td>
<td>In</td>
<td>-524.5</td>
<td>-335.6</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>Es 99</td>
<td>39.7</td>
<td>In</td>
<td>-533.6</td>
<td>-344.7</td>
<td>23.4</td>
<td></td>
</tr>
<tr>
<td>EuII 63</td>
<td>-329.8</td>
<td>In</td>
<td>-514.0</td>
<td>-325.1</td>
<td>21.4</td>
<td></td>
</tr>
<tr>
<td>EuIII 63</td>
<td>346.5</td>
<td>In</td>
<td>-502.2</td>
<td>-313.3</td>
<td>16.5</td>
<td></td>
</tr>
<tr>
<td>Fe 26</td>
<td>109.8</td>
<td>On</td>
<td>-286.5</td>
<td>-97.6</td>
<td>-207.4</td>
<td></td>
</tr>
<tr>
<td>Fl 100</td>
<td>-357.3</td>
<td>In</td>
<td>-534.2</td>
<td>-345.3</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Ga 31</td>
<td>11.7</td>
<td>In</td>
<td>-184.6</td>
<td>4.3</td>
<td>-7.4</td>
<td></td>
</tr>
<tr>
<td>Gd 64</td>
<td>-346.5</td>
<td>In</td>
<td>-524.7</td>
<td>-335.8</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>Ge 32</td>
<td>41.7</td>
<td>In (on)</td>
<td>-179.0 (-252.9)</td>
<td>9.9 (-64.0)</td>
<td>-31.8 (-105.7)</td>
<td></td>
</tr>
<tr>
<td>Hf 72</td>
<td>-266.3</td>
<td>In</td>
<td>-477.0</td>
<td>-288.1</td>
<td>-21.8</td>
<td></td>
</tr>
<tr>
<td>Hg 80</td>
<td>1.7</td>
<td>In</td>
<td>-191.7</td>
<td>-2.8</td>
<td>-4.4</td>
<td></td>
</tr>
<tr>
<td>Ho 67</td>
<td>-341.0</td>
<td>In</td>
<td>-523.2</td>
<td>-334.3</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>In 49</td>
<td>-25.8</td>
<td>In</td>
<td>-219.5</td>
<td>-30.6</td>
<td>-4.8</td>
<td></td>
</tr>
<tr>
<td>Ir 77</td>
<td>78.0</td>
<td>On</td>
<td>-353.8</td>
<td>-164.9</td>
<td>-242.9</td>
<td></td>
</tr>
<tr>
<td>K 19</td>
<td>-167.1</td>
<td>In</td>
<td>-342.3</td>
<td>-153.4</td>
<td>13.7</td>
<td></td>
</tr>
<tr>
<td>La 57</td>
<td>-333.4</td>
<td>In</td>
<td>-523.5</td>
<td>-334.6</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>Li 3</td>
<td>-192.1</td>
<td>In</td>
<td>-371.0</td>
<td>-182.1</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Mg 12</td>
<td>-89.0</td>
<td>In</td>
<td>-286.5</td>
<td>-97.6</td>
<td>-8.5</td>
<td></td>
</tr>
<tr>
<td>Mn 25</td>
<td>-53.8</td>
<td>In</td>
<td>-279.7</td>
<td>-90.8</td>
<td>-37</td>
<td></td>
</tr>
<tr>
<td>Mo 42</td>
<td>134.6</td>
<td>On</td>
<td>-327.4</td>
<td>-138.5</td>
<td>-273.1</td>
<td></td>
</tr>
<tr>
<td>Na 11</td>
<td>-155.2</td>
<td>In</td>
<td>-333.7</td>
<td>-144.8</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td>Nb 41</td>
<td>-41.2</td>
<td>In (on)</td>
<td>-286.4 (-407.7)</td>
<td>-97.4 (-218.8)</td>
<td>-56.2 (-177.6)</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2.17. Calculated values for the partial molar enthalpy of solution of polonium in solid elements B at infinite dilution, mechanism of polonium adsorption on/in solid surfaces of element B, see [Neuhausen, 2003], partial molar enthalpies of adsorption of polonium in/on solid surfaces of B at zero coverage, partial molar net enthalpies of adsorption of polonium in/on solid surfaces of B at zero coverage and partial molar enthalpies of segregation of polonium in a solid matrix of B (cont.)

<table>
<thead>
<tr>
<th>Element B</th>
<th>Atomic number Z</th>
<th>$\Delta H_{\text{ads}}^{\text{Po in B (s)}}$ (calc.) [kJmol$^{-1}$]</th>
<th>Adsorption mechanism</th>
<th>$\Delta H_{\text{ads}}^{\text{Po in/on B}}$ (calc.) [kJmol$^{-1}$]</th>
<th>$\Delta H_{\text{ads, net}}^{\text{Po in/on B}}$ (calc.) [kJmol$^{-1}$]</th>
<th>$\Delta H_{\text{seg}}^{\text{Po}}$ (calc.) [kJmol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd 60</td>
<td>-349.0</td>
<td>In</td>
<td>-522.1</td>
<td>-333.2</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td>Ni 28</td>
<td>41.7</td>
<td>In (on)</td>
<td>-201.6 (-325.6)</td>
<td>-12.7 (-136.7)</td>
<td>-54.4 (-178.4)</td>
<td></td>
</tr>
<tr>
<td>Np 93</td>
<td>-207.8</td>
<td>In</td>
<td>-395.3</td>
<td>-206.4</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>Os 76</td>
<td>146.4</td>
<td>On</td>
<td>-361.3</td>
<td>-172.4</td>
<td>-318.8</td>
<td></td>
</tr>
<tr>
<td>P 15</td>
<td>109.5</td>
<td>On</td>
<td>-191.3</td>
<td>-2.4</td>
<td>-111.9</td>
<td></td>
</tr>
<tr>
<td>Pa 91</td>
<td>-401.2</td>
<td>In</td>
<td>-583.4</td>
<td>-394.5</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>Pb 82</td>
<td>10.2</td>
<td>In</td>
<td>-207.3</td>
<td>-18.4</td>
<td>-8.2</td>
<td></td>
</tr>
<tr>
<td>Pd 46</td>
<td>-105.5</td>
<td>In</td>
<td>-327.1</td>
<td>-138.2</td>
<td>-32.6</td>
<td></td>
</tr>
<tr>
<td>Pr 61</td>
<td>-349.3</td>
<td>In</td>
<td>-522.9</td>
<td>-334</td>
<td>15.3</td>
<td></td>
</tr>
<tr>
<td>Po 84</td>
<td>0</td>
<td>In</td>
<td>-196.8</td>
<td>-7.9</td>
<td>-7.9</td>
<td></td>
</tr>
<tr>
<td>Pt 78</td>
<td>-21.2</td>
<td>In</td>
<td>-255.0</td>
<td>-66.1</td>
<td>-44.9</td>
<td></td>
</tr>
<tr>
<td>Pd 94</td>
<td>-296.7</td>
<td>In</td>
<td>-474.7</td>
<td>-285.8</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>Rb 37</td>
<td>-171.7</td>
<td>In</td>
<td>-345.9</td>
<td>-157</td>
<td>14.7</td>
<td></td>
</tr>
<tr>
<td>Re 75</td>
<td>188.8</td>
<td>On</td>
<td>-341.9</td>
<td>-153</td>
<td>-341.8</td>
<td></td>
</tr>
<tr>
<td>Rh 45</td>
<td>14.7</td>
<td>In</td>
<td>-231.1</td>
<td>-42.2</td>
<td>-56.9</td>
<td></td>
</tr>
<tr>
<td>Ru 44</td>
<td>115.2</td>
<td>On</td>
<td>-329.6</td>
<td>-140.7</td>
<td>-255.9</td>
<td></td>
</tr>
<tr>
<td>S 16</td>
<td>-41.0</td>
<td>In</td>
<td>-234.9</td>
<td>-46</td>
<td>-4.9</td>
<td></td>
</tr>
<tr>
<td>Sb 51</td>
<td>10.2</td>
<td>In</td>
<td>-194.2</td>
<td>-5.3</td>
<td>-15.5</td>
<td></td>
</tr>
<tr>
<td>Sc 21</td>
<td>-329.5</td>
<td>In</td>
<td>-518.4</td>
<td>-329.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Se 34</td>
<td>5.1</td>
<td>In</td>
<td>-194.1</td>
<td>-5.2</td>
<td>-10.3</td>
<td></td>
</tr>
<tr>
<td>Sn 14</td>
<td>105.6</td>
<td>On</td>
<td>-260.7</td>
<td>-71.8</td>
<td>-177.4</td>
<td></td>
</tr>
<tr>
<td>Sr 38</td>
<td>-336.6</td>
<td>In</td>
<td>-503.3</td>
<td>-314.4</td>
<td>22.2</td>
<td></td>
</tr>
<tr>
<td>Ta 73</td>
<td>-52.0</td>
<td>In</td>
<td>-307.8</td>
<td>-118.9</td>
<td>-66.9</td>
<td></td>
</tr>
<tr>
<td>Tc 65</td>
<td>-343.8</td>
<td>In</td>
<td>-523.4</td>
<td>-334.5</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>Tb 43</td>
<td>106.9</td>
<td>on</td>
<td>-314.1</td>
<td>-125.2</td>
<td>-232.1</td>
<td></td>
</tr>
<tr>
<td>Te 52</td>
<td>14.9</td>
<td>In</td>
<td>-187.2</td>
<td>1.7</td>
<td>-13.2</td>
<td></td>
</tr>
<tr>
<td>Th 90</td>
<td>-353.5</td>
<td>In</td>
<td>-537.5</td>
<td>-348.6</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>Ti 22</td>
<td>-183.7</td>
<td>In</td>
<td>-397.8</td>
<td>-208.9</td>
<td>-25.2</td>
<td></td>
</tr>
<tr>
<td>Tl 81</td>
<td>-24.8</td>
<td>In</td>
<td>-220.6</td>
<td>-31.7</td>
<td>-6.8</td>
<td></td>
</tr>
<tr>
<td>Tm 69</td>
<td>-340.8</td>
<td>In</td>
<td>-524.8</td>
<td>-335.9</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>U 92</td>
<td>-235.3</td>
<td>In</td>
<td>-428.0</td>
<td>-239.1</td>
<td>-3.7</td>
<td></td>
</tr>
<tr>
<td>V 23</td>
<td>-27.2</td>
<td>In</td>
<td>-269.7</td>
<td>-80.8</td>
<td>-53.6</td>
<td></td>
</tr>
<tr>
<td>W 74</td>
<td>182.7</td>
<td>On</td>
<td>-354.3</td>
<td>-165.4</td>
<td>-3.48</td>
<td></td>
</tr>
<tr>
<td>Y 39</td>
<td>-346.5</td>
<td>In</td>
<td>-527.9</td>
<td>-339</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>YbII 70</td>
<td>-327.5</td>
<td>In</td>
<td>-501.3</td>
<td>-312.4</td>
<td>15.1</td>
<td></td>
</tr>
<tr>
<td>YbIII 70</td>
<td>-340.8</td>
<td>In</td>
<td>-510.2</td>
<td>-321.3</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>Zn 30</td>
<td>14.7</td>
<td>In</td>
<td>-192.6</td>
<td>-3.7</td>
<td>-18.4</td>
<td></td>
</tr>
<tr>
<td>Zr 40</td>
<td>-320.1</td>
<td>In</td>
<td>-517.2</td>
<td>-328.3</td>
<td>-8.2</td>
<td></td>
</tr>
</tbody>
</table>
5.3 Investigations on irradiated LBE

5.3.1 Release of volatile radionuclides

In a critical system the production of radionuclides will be limited to isotopes near that of the target material. These elements will include polonium and mercury. However, in a spallation target using liquid LBE as a target material, isotopes of practically all chemical elements, ranging from hydrogen up to polonium, will be produced by different nuclear reactions. Among these nuclear reaction products there will be several elements which have to be considered more or less volatile at the operation conditions of the target. Table 5.3.1 lists the total inventory of the most important volatile elements which would be expected for a 200 d irradiation of the MEGAPIE target planned to be irradiated at PSI with 1.4 mA of 575 MeV protons based on the results of neutronics calculations using FLUKA and ORIHET3 [Zanini, 2005]. Among these elements, polonium and mercury have to be considered the most relevant from the radiation protection point of view. While polonium as an α-emitter is problematic mainly because of its high radiotoxicity, the importance of mercury arises from the fact that it is the element produced at largest quantities and, at the same time, it is the element with the by far highest volatility.

### Table 5.3.1. Production of volatile elements within the MEGAPIE target calculated using the FLUKA/ORIHET3 codes for an irradiation with 1.4 mA of 575 MeV protons for 200 days

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass produced m [g]</th>
<th>Mole fraction in target x</th>
<th>Total activity [Bq]</th>
<th>n produced [mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Po</td>
<td>2.9</td>
<td>3.3*10^-6</td>
<td>1.1*10^15</td>
<td>1.4*10^-2</td>
</tr>
<tr>
<td>Bi</td>
<td>79.5</td>
<td>0.553</td>
<td>4.3*10^15</td>
<td>3.8*10^-1</td>
</tr>
<tr>
<td>Pb</td>
<td>100</td>
<td>0.447</td>
<td>5.7*10^15</td>
<td>4.9*10^-1</td>
</tr>
<tr>
<td>Tl</td>
<td>7.5</td>
<td>8.9*10^-6</td>
<td>4.5*10^15</td>
<td>3.7*10^-2</td>
</tr>
<tr>
<td>Hg</td>
<td>18.9</td>
<td>2.3*10^-5</td>
<td>1.5*10^15</td>
<td>9.5*10^-2</td>
</tr>
<tr>
<td>Xe</td>
<td>2.0*10^-2</td>
<td>3.8*10^-8</td>
<td>2.1*10^-2</td>
<td>1.6*10^-4</td>
</tr>
<tr>
<td>I</td>
<td>8.9*10^-2</td>
<td>1.7*10^-8</td>
<td>5.8*10^-2</td>
<td>7.0*10^-3</td>
</tr>
<tr>
<td>Cs</td>
<td>1.4*10^-1</td>
<td>2.5*10^-9</td>
<td>2.8*10^-2</td>
<td>1.0*10^-3</td>
</tr>
<tr>
<td>Cd</td>
<td>1.9*10^-1</td>
<td>4.1*10^-1</td>
<td>7.2*10^-2</td>
<td>1.7*10^-3</td>
</tr>
<tr>
<td>Rb</td>
<td>1.6*10^-1</td>
<td>4.7*10^-1</td>
<td>1.9*10^-3</td>
<td>2.0*10^-4</td>
</tr>
<tr>
<td>Br</td>
<td>7.5*10^-2</td>
<td>2.1*10^-1</td>
<td>3.7*10^-5</td>
<td>8.8*10^-4</td>
</tr>
<tr>
<td>I</td>
<td>3.4*10^-2</td>
<td>1.0*10^-1</td>
<td>2.6*10^-3</td>
<td>4.2*10^-4</td>
</tr>
</tbody>
</table>

For radioprotection issues it is important to assess the behaviour of these elements during normal and off-normal operation conditions. In the following, we will discuss evaporation for the case of the MEGAPIE target as an example.

Under normal operating conditions a certain fraction of each volatile element will be evaporated to the cover gas of the target. In the following, we assume that the maximum vapour phase concentration that can be reached by release from LBE to the gas phase corresponds to the equilibrium vapour pressure, which can be calculated according to:

\[
p_A = \gamma_A x_A p_A^o
\]  

(5.26)

where \(p_A\) is the equilibrium vapour pressure of the component A over the mixture, \(x_A\) is the mole fraction of the dissolved component A, \(\gamma_A\) is the thermodynamic activity coefficient of the dissolved component A and \(p_A\) is the vapour pressure of the pure component A.
Assuming ideal behaviour of the gaseous phase, the amount \( n \) (in moles) of volatiles in the gas phase of the expansion tank can then be calculated by:

\[
n_A = \frac{p_AV}{RT} \quad (5.27)
\]

where \( n_A \) is the amount of volatile A in the gas phase (moles), \( p \) is the vapour pressure of the volatile A (Pa), \( V \) is the cover gas volume \( (m^3) \), \( R \) is the universal gas constant \( (8.314 \text{ Jmol}^{-1}\text{K}^{-1}) \) and \( T \) is the temperature in K.

The behaviour of volatiles in off-normal conditions will depend on the actual accident scenario and may include interaction with air, water and cooling liquids. A simple method for the estimation of maximum release rates will be given in Section 5.3.3.

### 5.3.1.1 Polonium vaporisation

For polonium, different vapour species and vaporisation reactions have been discussed in literature. The most prominent of these species are \( \text{PbPo} \) and \( \text{H}_2\text{Po} \). \( \text{BiPo} \) or \( \text{Po}_2 \) molecules have not received much consideration. Given the actual state of research on polonium release from LBE we cannot be sure which of the above mentioned species would be the prominent form of polonium to be released from the liquid LBE. However, for an assessment of the source terms for polonium release in normal operation as well as in accident scenarios, this question does not have to be answered as long as a quantification of polonium in the gas phase is possible as a function of operating conditions such as temperature and composition. For this purpose, we can rely on experimental data in comparison with values obtained by extrapolation of thermodynamical functions [Eichler, 2002] and semi-empirical calculations [Neuhausen, 2003]. As most of the available experimental data are based on measurements performed at higher temperatures, we have to rely on extrapolations to lower temperature to assess the behaviour at the typical operating condition—approximately 450 to 650 K.

In the following we will discuss data on polonium release from liquid metals obtained by different authors. In general, experimental results on polonium release from liquid metals such as Bi or LBE show that much lower vapour pressures or evaporation rates are found for polonium dissolved in Bi [Joy, 1963] or LBE [Tupper, 1991], [Buongiorno, 2003], [Neuhausen, 2004] than would be expected from literature values for the vapour pressure of pure polonium [Brooks, 1955], [Abakumov, 1974]. This indicates that the thermodynamic activity coefficient for polonium in liquid Bi or LBE solution is <1. Figure 5.3.1 shows a comparison of values for the effective vapour pressure of polonium at a mole fraction of \( 3.3 \times 10^{-6} \) in LBE solution (MEGAPIE target after an irradiation of 200 d with 1.4 mA of 572 MeV protons) obtained from different studies as well as from experiments performed at PSI.

Joy studied the vapour-liquid equilibrium of dilute solutions of polonium in liquid bismuth \( (x \approx 10^{-6} \text{ to } 10^{-10}) \) under vacuum [Joy, 1963]. From his experimental data he derived the following relation for the thermodynamic activity coefficient of dilute polonium in bismuth for the temperature range between 723 and 1123 K based on the vapour pressure relation obtained for the temperature range between 711 and 1018 K from [Brooks, 1955]:

\[
\log \gamma_{\text{po}} = -2728.3/T[K] + 1.1176 \quad (5.28)
\]

\[
\log p_{\text{po}}[\text{Torr}] = -5377.8/T[K] + 7.2345 \quad (5.29)
\]
Figure 5.3.1. Effective vapour pressure of polonium over a diluted solution (x = 3.3×10−6) of polonium in bismuth [Joy, 1963], [Brooks, 1955]) or LBE [Buongiorno, 2003], [Neuhausen, 2004], together with theoretically derived data. Values corresponding to the temperature regime experimentally investigated are depicted as full symbols, while extrapolated data are shown as open symbols.

Eq. (5.26) was used to calculate the vapour pressure of polonium above a solution with a mole fraction of 3.3×10−6 for polonium in liquid bismuth. The corresponding values are shown as diamonds in Figure 5.3.1. We assume that the chemical interactions of polonium with liquid bismuth and LBE are similar. Hence, the thermodynamic activity coefficients should be of a comparable magnitude and the results can be used for an evaluation of polonium in LBE.

[Buongiorno, 2003] studied the equilibrium vapour pressure of polonium over LBE (x ≈ 10−8) in the temperature range from 665 to 823 K in an argon atmosphere. They obtained the following vapour pressure relation as a function of temperature:

\[ \log p_{Po(\text{eff})}[\text{Torr}] = -6790/T[\text{K}] + 6.64 \]  \hfill (5.30)

In this equation, an error introduced by the incorrect calculation of mole fraction values by the authors has been corrected. Since this equation corresponds to an effective vapour pressure over an LBE solution of polonium, where the thermodynamic activity coefficient is already included, we can calculate the vapour pressure for MEGAPIE conditions by multiplying the vapour pressure obtained using Eq. (5.30) with the mole fraction of 3.3×10−6 expected at the end of irradiation. The resulting values are plotted as triangles in Figure 5.3.1.

The release of polonium from liquid LBE has been studied at PSI under an Ar/7%H₂ atmosphere as a function of temperature using carrier free amounts of polonium (x ≈ 10−12) [Neuhausen, 2004]. In these experiments the amount of polonium transported from a LBE sample under a constant gas flow during a constant time was determined (see Section 5.3.2). Evaluating the amount of polonium transported, an effective vapour pressure of polonium can be estimated using the perfect gas law. The
relation for this effective vapour pressure of polonium over liquid LBE derived from the results of release experiments between 1011 and 1167 K is given in Eq. (5.31):

$$\log p_{\text{Po}(\text{eff})} \, [\text{Torr}] = -\frac{7158}{T} \, [\text{K}] + 6.82 \tag{5.31}$$

By multiplying with the mole fraction expected for MEGAPIE we arrive at the values plotted as circles in Figure 5.3.1.

Eichler derived a consistent set of thermodynamic data for polonium (enthalpy, entropy, Gibbs energy) from extrapolations within the chalcogen group (see Section 5.2.1) [Eichler, 2002]. Based on these data, temperature functions for the vapour pressure of polonium have been derived for the evaporation of monoatomic polonium as well as diatomic Po$_2$ molecules. According to these data, Po$_2$ molecules should be the dominating species over pure polonium at temperatures relevant to MEGAPIE. For this reason we include in Figure 5.3.1 the vapour pressure of Po$_2$ over a solution with a mole fraction of $3.3 \times 10^{-6}$ calculated from the vapour pressure function derived from thermodynamic functions [Eichler, 2002] and an estimation for the thermodynamic activity coefficient. The thermodynamic activity coefficient can be calculated from the following relation:

$$\Delta G_{\text{ex}} \, (\text{Po in M}) = RT \ln \gamma \tag{5.32}$$

where $\Delta G_{\text{ex}} \, (\text{Po in M})$ is the partial molar excess Gibbs free energy for the solution of polonium in a liquid metal, and:

$$\Delta G_{\text{ex}} \, (\text{Po in Pb}) = \Delta H_{\text{ex}} \, (\text{Po in M}) - T \Delta S_{\text{ex}} \, (\text{Po in M}) \tag{5.33}$$

where $\Delta H_{\text{ex}}$ and $\Delta S_{\text{ex}}$ are the corresponding excess enthalpies and entropies. While $\Delta S_{\text{ex}}$ is not known, $\Delta H_{\text{ex}}$ corresponds to the partial molar enthalpy of solution of polonium in liquid metals. The latter has been calculated in [Neuhausen, 2003] using the Miedema model. As a first approximation we use $\Delta H_{\text{ex}}$ as an approximation for $\Delta G_{\text{ex}}$ and neglect its temperature dependency. Based on Eq. (5.29) and the value of -10.2 kJ/mol for $\Delta H_{\text{ex}}$ for polonium in liquid lead [Neuhausen, 2003] we obtain an activity coefficient of $\gamma = 0.016$ at 298 K.

For Po$_2$ over pure liquid polonium, the following vapour pressure relation has been obtained from extrapolated thermodynamic data [Eichler, 2002]:

$$\log p_{\text{Po}_2} \, [\text{Torr}] = -7584.1/T \, [\text{K}] + 9.2795 \tag{5.34}$$

Together with the values of mole fraction $x = 3.3 \times 10^{-6}$ and activity coefficients calculated using Eq. (5.32) we calculate effective vapour pressures displayed as crosses in Figure 5.3.1.

The four curves show satisfactory agreement. This is valid especially in the temperature range between 1000 and 600 K. For a conservative assessment of polonium release we choose Eq. (5.30) because it gives the highest values for polonium vapour phase concentrations in the temperature region of interest for MEGAPIE.

An increase of polonium gas phase concentration has been observed when a mixture of hydrogen and water is bubbled through LBE [Buongiorno, 2003]. This effect has been attributed to the formation of polonium hydride, H$_2$Po. The experimental results were interpreted in terms of values for the Gibbs free energy change $\Delta G$ for the following reactions:
\[
PbPo(s) + H_2O(g) \leftrightarrow H_2Po(g) + PbO \quad (5.35)
\]
\[
\Delta G \ [kJmol^{-1}] = (17.0 \pm 4.1) + (0.150 \pm 0.007) \times T[K] \quad (5.36)
\]

and:

\[
H_2 + PbPo \leftrightarrow H_2Po + Pb \quad (5.37)
\]
\[
\Delta G \ [kJmol^{-1}] = -(7.90 \pm 4.1) + (0.103 \pm 0.007) \times T \ [K] \quad (5.38)
\]

From these relations, the gas phase concentration of H\(_2\)Po can be calculated using the relation between \(\Delta G\) and the equilibrium constant \(K\):

\[
\Delta G = -RT\ln K \quad (5.39)
\]

where:

\[
K = \frac{cPbO \times cH_2Po}{cPbPo \times cH_2O} \text{ for reaction (5.40)}
\]

and:

\[
K = \frac{cH_2Po \times cPb}{cH_2 \times cPbPo} \text{ for reaction (5.41)}
\]

concentrations \(c\) are given in mol/l for all components and phases in [Buongiorno, 2003] and thermodynamic activity coefficients have been set as 1.

For reaction (5.35) we obtain:

\[
c(H_2Po) = K \times c(H_2O) \times \frac{c_{PbPo}}{c_{PbO}} \quad (5.42)
\]

and for reaction (5.37):

\[
c(H_2Po) = K \times c(H_2) \times \frac{c_{PbPo}}{c_{Pb}} \quad (5.43)
\]

The temperature functions for \(\Delta G\) given in [Buongiorno, 2003] disagree with thermodynamic data for H\(_2\)Po and PbPo derived in an extrapolative manner using the periodicity within the chalcogen group [Eichler, 2004a]. The latter are in reasonable agreement with formation energies of H\(_2\)Po and PbPo calculated using quantum mechanical methods [Mavridis, 2005], [Neuhausen, 2003] and would give rise to much lower H\(_2\)Po gas phase concentrations. On the contrary, the formation of H\(_2\)Po has been reported by other groups [Pankratov, 1999 and references cited therein]. However, H\(_2\)Po is reported to be unstable in humid air. A 94% decay of H\(_2\)Po in humid air at 289 K was reported in [Pankratov, 1999]. Overall, the knowledge concerning formation and stability of H\(_2\)Po is not sufficient for a reliable evaluation of its importance for polonium release from LBE. For example, the higher gas phase concentrations of polonium observed in [Buongiorno, 2003] could also originate from the formation of LBE aerosols carrying polonium activity. Further study is necessary to clarify the situation.

5.3.1.2 Evaporation characteristics of polonium and its lighter homologues selenium and tellurium from liquid Pb-Bi eutecticum

Gamma-active isotopes of polonium and its lighter homologues selenium and tellurium were implanted into LBE samples at CERN-ISOLDE [Neuhausen, 2004]. The evaporation behaviour of
these elements dissolved in liquid LBE has been studied at various temperatures in the range from 482 K up to 1330 K under a continuous flow of Ar/H₂ or Ar/H₂O using γ-ray spectroscopy.

Polonium release in the temperature range of interest for technical applications is slow. Within short term (1 h) experiments measurable amounts of polonium are evaporated only at temperatures above 973 K as is shown in Figure 5.3.2. Long term experiments reveal that a slow evaporation of polonium occurs at temperatures around 873 K resulting in a fractional polonium loss of the melt of around 1% per day as shown in Figure 5.3.3. Evaporation rates of selenium and tellurium are smaller than those of polonium. The presence of H₂O does not enhance the evaporation within the error limits of experiments as illustrated in Figure 5.3.4. The thermodynamics and possible reaction pathways involved in polonium release from LBE are discussed in more detail in [Neuhausen, 2004] and [Eichler, 2004a].

Figure 5.3.2. Comparison of the release behaviour of selenium, tellurium and polonium from LBE (1 h experiments) in an Ar/7%-H₂ atmosphere as a function of temperature

Figure 5.3.3. Comparison of the long-term polonium release from LBE in an Ar/7%-H₂ atmosphere at different temperatures as a function of heating time
5.3.2 Thermal release behaviour of mercury and thallium from liquid eutectic lead-bismuth alloy

LBE samples have been irradiated with neutrons in SINQ at PSI, where mercury and thallium nuclides are formed by (n, xn) reactions of the sample materials and subsequent electron capture or β+ decay of Pb and Bi nuclides as well as (n, α) reactions [Neuhausen, 2005a].

The release of mercury and thallium from liquid LBE under a flowing Ar/7%-H₂ atmosphere has been studied in the temperature range from 408 to 1292 K using γ-ray spectroscopy [Neuhausen, 2005a]. For technical applications such as liquid metal spallation targets or accelerator-driven systems, where liquid LBE is planned to be used as the target material, the release of radioactive mercury isotopes produced by spallation is expected to be one of the major safety issues.

During short-term experiments, significant amounts of mercury begin to evaporate from liquid LBE at temperatures starting from about 475 K as shown in Figure 5.3.5. 80% of the mercury present in the sample is released from samples of approximately 1.5-3 g within one hour at temperatures higher than 625 K. Thallium release in the temperature range investigated is below experimental error. Long-term experiments reveal that even at temperatures as low as 476 K about 25% of the mercury present in the samples is released per day under a flowing Ar/7%-H₂ atmosphere as shown in Figure 5.3.6.

Further studies of Hg release were conducted using realistic concentrations of Hg and various gas atmospheres ranging from reducing to oxidising conditions [Neuhausen, 2006]. The main results are depicted in Figure 5.3.7. Under reducing conditions, substantial release of mercury from LBE starts at temperatures around 473 K. At about 571 K, half of the mercury present in the samples is released within one hour. The good agreement between results for carrier-free (mole fraction ≈ 10⁻¹²) and higher concentration (mole fraction ≈ 6*10⁻⁵) samples suggest that Henry’s law is valid for the behaviour of Hg in LBE within this concentration range.
Figure 5.3.5. Fractional release of mercury and thallium from LBE (1 h experiments) in Ar/7%-H₂ atmosphere as a function of temperature

Figure 5.3.6. Comparison of the long-term mercury and thallium release from LBE in an Ar/7%-H₂ atmosphere at different temperatures as a function of the square root of heating time

Figure 5.3.7. Comparison of the fractional release of Hg from liquid LBE under different gas atmospheres and different Hg concentrations
Oxidising conditions lead to a strong decrease of mercury release. In 1 h experiments, no release of mercury is observed for temperatures up to 935 K within the limits of experimental error when humid air is used as carrier gas. Apparently, the formation of an oxide layer on the surface of the melt inhibits the evaporation of Hg. This effect is of importance with respect to accident scenarios in liquid metal spallation targets, where liquid LBE could be exposed to air as well as cooling water. In such a case, a substantial decrease of the evaporation rate of mercury can be expected due to the formation of an oxide layer.

The use of noble metal absorbers for the fixation of mercury released to the gas phase has been examined in a preliminary study [Eichler, 2004b].

5.3.3 Release of volatile radionuclides in abnormal operating conditions

Different accident scenarios have been considered to estimate the hazards of a failure during the operation of a liquid metal system [Perret, 2002]. Many of these scenarios have a common feature: A surface of hot LBE will be exposed to an atmosphere containing oxygen and possibly water vapour from the evaporation of cooling water, which also can leak from the target system in case of a failure. Volatiles will be evaporated from the hot LBE surfaces to the target containment until LBE is solidified. A fraction of these volatiles may be released to the environment in case an interlinkage between the target containment and the environment is formed during the accident. The oxygen in the atmosphere will have an influence on the release behaviour. First of all, lead and bismuth oxides will form on the surface of LBE. This surface oxide layer can drastically decrease the release rate. Furthermore, the presence of oxygen shifts the hydrogen/water equilibrium \( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \) to the product side. Thus, release reactions that involve hydrogen containing volatile species, e.g. \( \text{H}_2\text{Po} \), will be suppressed.

In this section, a simple general procedure to estimate the maximum release of volatiles from a given LBE surface is shown. Parameters like the area of the LBE surface as well as its temperature as a function of time have to be specified. This approach only considers the maximum amount of volatiles to be released from such an LBE surface. The fraction of these volatiles that will be finally transported to the environment is not considered.

The following equation for the maximum evaporation rate of a metal into vacuum was derived by Langmuir from kinetic gas theory [Langmuir, 1913]:

\[
R_m = 0.0583 \times p^* \times \sqrt{\frac{M}{T}}
\]  

(5.44)

where \( R_m \) is the evaporation rate [g cm\(^{-2}\) s\(^{-1}\)], \( p^* \) is the vapour pressure of pure metal [Torr] and \( M \) is the atomic/molecular mass [g mol\(^{-1}\)].

Evaporation rates observed in practice under non-vacuum conditions typically are considerably lower [McNeese, 1967] due to collisions of the evaporating particles with molecules of the gas phase.

For a component \( A \) in a dilute mixture, the vapour pressure of the pure metal is replaced by its vapour pressure over the dilute solution

\[
p_A = \gamma_A x_A p_A^*
\]

(5.45)

where \( p_A \) is the vapour pressure of the component \( A \) over the mixture [Torr], \( x_A \) is the mole fraction of the dissolved component \( A \), \( \gamma_A \) is the thermodynamic activity coefficient of the dissolved component \( A \) and \( p_A \) is the vapour pressure of the pure component \( A \) [Torr].
Hence:

\[ R_{mA} = 0.0583 \gamma_A \sqrt{M/T} \quad \text{[gcm}^{-2}\text{s}^{-1}] \quad (5.46) \]

As a conservative approach, it is recommended that Eq. (5.46) be used to assess the evaporation of volatiles for accident scenarios in cases where experimental data on release rates are not available.

For mercury [Greene] and polonium [Tupper, 1991] experimental investigations on release rate have been performed. The results of these investigations can be used to assess the release of these two most important volatiles. A quantitative evaluation [Neuhausen, 2005b] of polonium release experiments performed at PSI [Neuhausen, 2004] confirmed the release rates measured in [Tupper, 1991]. These data are plotted in Figure 5.3.8. From these evaluations, the following temperature function for the release rate of polonium was derived:

\[ \log R_m/x = 0.97 \pm 0.22 - 6049 \pm 200/T \quad (5.47) \]

with a correlation coefficient of 0.99352, and where \( R_m \) is the mass release rate of polonium [gcm\(^{-2}\)s\(^{-1}\)], \( x \) is the mole fraction of polonium and \( T \) is the temperature in K.

This function can be used for the calculation of evaporation rates under various accident scenarios.

\[ \text{Figure 5.3.8. Comparison of Po release rate from liquid LBE normalised to Po mole fraction measured in different experiments [Neuhausen, 2005b]} \]

A preliminary study of polonium removal from contaminated quartz plates is described in [Obara, 2003]. Contamination of quartz plates was achieved by deposition of Po-contaminated LBE evaporated at approximately 1273 K. The deposition took place at about 873 K under an argon atmosphere. Polonium was selectively removed from the quartz plates in vacuum at 573 K, leaving the non-radioactive fraction of the deposited material on the quartz surface.
5.4 Irradiation effects

5.4.1 Measurement of gas and volatile element production rates in a proton-irradiated molten lead-bismuth target in the ISOLDE facility

5.4.1.1 ISOLDE facility and proton beam

A knowledge of the production rate and of the release properties of stable and radioactive volatile elements produced during operation of a spallation target is essential. A liquid spallation target comprises new design challenges which must be faced in view of the construction of a full-scale ADS prototype. One of the aspects that must be considered in the design of the MEGAPIE target is how to handle the gas produced during operation. Following the interaction of the high-energy proton beam with the target, nuclides are produced, many of which have high volatility. As an indication, a list of elements with high volatility is given in [Köster, 2001]. The elements are classified on the basis of the temperature at which the vapor pressure reaches 0.01 mbar. The products with high volatility are H, He, N, O, F, Ne, Cl, Ar, Br, Kr, I, Xe, Hg and At. The products with lower volatility, but still significant at the operating temperatures of the MEGAPIE experiment, are Na, P, S, K, Zn, As, Se, Rb, Cd, Te, Cs, and Po.

An experiment was conducted to study the production rates of stable and radioactive volatile elements in a LBE target irradiated by a proton beam of the energy of the order of 1 GeV. In this section the experiment is described and initial results are shown.

The experiment was performed at the ISOLDE facility [Kugler, 2000]. A schematic view is shown in Figure 5.4.1. The facility is connected to the PS booster (PSB), consisting of four small synchrotrons. Protons from a linac are pre-accelerated to 1 GeV or 1.4 GeV, before being injected to the 27 GeV proton synchrotron.

![Figure 5.4.1. Schematic view of ISOLDE hall](image)

The PSB provides one pulse of $3.2 \times 10^{13}$ protons every 1.2 seconds. A supercycle is made up of a string of 12 pulses. Up to half of the pulses in a super cycle can be delivered to the ISOLDE target. The protons from the PS Booster are delivered to the targets via a 100 m long underground transfer.
The proton beam is sent either to the High Resolution Separator (HRS) target or to the General Purpose Separator (GPS) target. The proton beam energy in the experiment was of 1.4 GeV. In the experiment one pulse per super cycle (16.8 s) was used. Proton pulses of 1.4 GeV and variable intensity (up to $10^{13}$ protons/pulse with a rate of one pulse every 16.8 s) impinged on the target. Following the spallation reactions, the volatile elements produced and exiting the liquid metal were ionised by means of a plasma ion source, then accelerated to 60 keV and sent to the magnetic mass separators and to the beam lines where the measuring stations were located.

5.4.1.2 ISOLDE target

The spallation targets at ISOLDE are contained in special target units. Cylindrical tantalum containers, 20 cm long and with 1 cm radius, are filled with the target material. Tantalum is a heavy, hard and ductile metal most unlikely to react with most elements and with a high boiling point.

The target material was a LBE sample with mass of 547 grams. The measurements were performed with the target at temperatures of 400°C and 600°C. Temperature differences within these ranges are not expected to affect the releases of the noble gases and Hg isotopes. On the other hand, differences are expected for some isotopes such as I, Cd and Po.

Table 5.4.1 presents the parameters of the beam and target for the experiment.

Table 5.4.1. Summary of beam and target parameters for the ISOLDE experiment

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ISOLDE experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam energy</td>
<td>1.4 GeV</td>
</tr>
<tr>
<td>Beam pulse length</td>
<td>2.4 μs</td>
</tr>
<tr>
<td>Beam repetition rate</td>
<td>16.8 s</td>
</tr>
<tr>
<td>Beam current (average value)</td>
<td>$0.95 \times 10^{-4}$ mA (for $10^{13}$ ppp)</td>
</tr>
<tr>
<td>Beam profile (Gaussian)</td>
<td>$\sigma_x = \sigma_y = 3.5$ mm</td>
</tr>
<tr>
<td>LBE mass</td>
<td>547 g</td>
</tr>
<tr>
<td>Target size (cylindrical)</td>
<td>L = 20 cm, r = 1 cm</td>
</tr>
<tr>
<td>Target temperature at experiment</td>
<td>400°C, 600°C</td>
</tr>
<tr>
<td>Transfer line temperature</td>
<td>300°C</td>
</tr>
</tbody>
</table>

5.4.1.3 Measurement techniques

Yields were measured using three different techniques in common use at ISOLDE.

1) Online yields of stable as well as some radioactive isotopes were measured using a Faraday cup (FC) inserted in the beam line. A special data acquisition system was developed at PSI [Manfrin, 2004] to trigger the current measurement with the arrival of the proton beam on target, thus allowing the measurement of the gas release curves, characteristic of each element.

2) For short-lived $\beta$ emitting isotopes, beams were directed to a dedicated tape station and yields were measured with a plastic scintillator detector. The online measurement with the tape station allows correction for partial decay of isotopes produced inside the target, before the release. In fact, since the release is dependent on the chemical properties of a given element, it is possible for instance to fit the release functions of $^6$He (measured with the tape station) and $^4$He (measured with the Faraday cup) and correct for the partial decay of the $^6$He.
3) A third measurement method was used for longer-lived (T_{1/2} ≥ 5 min) γ-emitting radioisotopes; ion beams were implanted on thin Al foils at the measuring station, then after irradiation an offline γ detection was performed using a calibrated HPGe detector.

5.4.1.4 Data analysis

The release process of volatile elements

The release of the volatile elements from a molten metal target is a complex process [Köster, 2000]. The volatile species formed in the interaction process first diffuse in the liquid. The diffusion rates in the bulk material depend on the temperature and on the atomic mass. Following diffusion through the bulk material, the elements diffuse through the target container, the transfer line and the ion source. The effusion time is given by the number of wall collisions times the average time between two wall collisions. For a real target/ion source combination the total release time is given by a combination of the diffusion time and the effusion time.

The average release time for a volatile product from a liquid target is typically in the order of minutes, and decreases with increasing temperature.

The release profiles are typically described by a sum of two exponential decay terms multiplied by an exponential grow-in term as follows from [Köster, 2000]:

\[ p(t) = C(1 - \exp(-t/\tau_r))[\alpha \exp(-t/\tau_f) + (1 - \alpha)\exp(-t/\tau_s)] \]  \hspace{1cm} (5.48)

where \( \tau_r \) is the characteristic rise time, \( \tau_f \) and \( \tau_s \) are two decay times, fast and slow; \( \alpha \) is the relative contribution of the fast and slow components and \( C \) is a normalisation factor.

Almost all elements in these experiments are released with a fast peak component shorter than 6 seconds and a slow peak at longer times. Figures 5.4.2 and 5.4.3 show the release curves for \(^{80}\text{Kr}\) and \(^{196}\text{Hg}\) measured with the Faraday cup. The fast part of the release curve is easily identified as the peaks in the beginning of the curve. The small drop just before the big peak is a result of the fact that the high voltage supply is pulsed (to avoid possible break down following the beam impact), and is brought to zero 35 μs before beam impact, and then restored to the regular 60 kV value after 5 ms [Kugler, 2000].

Figure 5.4.2. \(^{80}\text{Kr}\) release function, measured with the LBE target at proton beam intensity of \(1 \times 10^{13}\) protons/pulse, during 6 seconds
The tail after the peak represents the slow component of the release function. The tail of the release function is longer than the cycle length of 16.8 seconds, and therefore the long components of the release function accumulate one on top of another, forming a background level that can be observed at the left of the main peak. Thus in order to measure the whole release one has to measure for an entire cycle length.

The drop in the middle of $^{80}$Kr release peak was probably due to fluctuations in the efficiency of the plasma ionisation source because of the pulsed beam. This is an effect that is dependent on the proton beam intensity. As far as its effect on determination of the production rate goes, this drop is not significant since the total release is dominated by the slow component.

The study of release functions is important for very short lived isotopes, like $^6$He. By comparing the release functions of $^4$He (measured with the tape station) and $^4$He (measured with the Faraday cup) the fraction of the decay of $^6$He before detection can be calculated.

Efficiency

The rate of particles detected $r$ can be described by the following relation [Köster, 2000]:

$$r = \Phi \sigma_{ind} N \varepsilon_{rel} \varepsilon_{ion} \varepsilon_{det}$$

(5.49)

where the $\Phi$ is the flux of the incident particles, the protons, $\sigma_{ind}$ the cross-section for producing a given isotope in the target and $N$ the number of target atoms exposed to the incident beam. Decay losses are included in all the efficiencies, and are only relevant for short-lived isotopes. One should note that the individual efficiencies correlate. For example if the efficiency of an ion source is improved, the emittance may worsen, thus reducing the transmission efficiency [Köster, 2000]. The release efficiency, $\varepsilon_{rel}$ is the fraction of the isotope that is released from the target after the spallation reaction. It is equal to one for the off-line results and plays only a role in the short-lived isotope measurements done with the tape station. All measured isotopes in the off-line measurements have half-lives long enough for not influencing the release efficiency.

The ionisation efficiency, $\varepsilon_{ion}$ is the fraction of the released isotopes that are really ionised, in the ion source. The ionisation efficiency is in fact a product of three different efficiencies: the ionisation efficiency, the extraction efficiency and the separator efficiency, but in this experiment they are considered as one unit. The transmission efficiency, $\varepsilon_{t}$ i.e. the fraction of the released and ionised isotopes that are transported to the measuring station. The detector efficiency, $\varepsilon_{det}$ i.e. the fraction of the emitting $\gamma$-rays (in the case of the $\gamma$-spectroscopy measurement) or $\beta$-radiation (in case of the tape station measurement) which are detected.
In order to obtain the absolute production rates from the measured yields, the efficiency of the ion source had to be measured. For this purpose, known amounts of different gas mixtures (consisting of Ar/Xe and He/Ne/Kr/Xe) were leaked into the ion source, allowing measurement of the efficiencies at any time during the experiment. For the other elements, the ion source efficiency was deduced (with somewhat larger errors) from the dependence on the ionisation potential and the mass of the isotopes, or from existing data in the literature. In the first test the ion source was injected with a mixture of 95% Ar and 5% Xe at 0.922 bar and in the second test it was filled with a mixture of 40% He, 20% Ne, 20% Kr and 20% Xe at 1.00 bar. A difference of about 30% between the two measurements indicates a probable small leakage of the ion source. Measured ionisation efficiencies for xenon were about 3.7%. The ionisation efficiency for mercury cannot be measured but results in [Kirchner, 1996] show an ionisation ratio of about a factor 1.5 for Hg+/Xe+. Using this ratio, we assumed an ionisation efficiency of 5.5% for Hg.

Additional corrections are needed for radioactive isotopes to account for their decay between the production time at the target and the detection time. The corrections are different for the tape station and the collection measurements. In this discussion we concentrate on the latter case, as well as on the Faraday cup measurement, for which no corrections are necessary since stable or long-lived isotopes are measured with this technique.

In most of the cases, a given nuclide can be formed not only by production following a spallation reaction, but also by the β decay of other isobaric nuclei, or by α decay. In this case what is measured is the cumulative cross-section, that is, the sum of the independent cross-section plus the contribution from the decaying parents. This contribution is usually very important. Ideally, the measurement should start when the contribution from decaying parents has reached a constant level (equilibrium conditions), so that the comparison with calculated values is easier. During the measurement, this was the case for most of the isotopes, with some exceptions especially for Hg isotopes.

Different transmission lines in the ISOLDE facility were used for the off-line and the on-line measurements. The transmission efficiency is about 90-95% for the off-line collection as well as for the FC and slightly lower, 88%, for the tape station.

Monte Carlo calculations

The Monte Carlo calculations were done using the codes FLUKA [Fasso, 2001] and MCNPX [Waters, 2002]. A simple model of the LBE target was used, as shown in Figure 5.4.4. A cylinder filled to 75% with LBE and bombarded by a 1.4 GeV proton beam was modelled. Although the geometry of the target is more complex, this simple modelling should be accurate enough to provide expected production rates. In fact, the target material is surrounded by the structure of the target holder, consisting essentially of Al and Cu. No difference should be expected by introducing these extra elements, as they are not moderating materials. The only moderating material is placed about 1 m away from the target, and is the marble beam dump. The isotope production rate in the target was calculated in atoms/μC.

Figure 5.4.4. Calculation model used in the Monte Carlo programs
For the MCNPX calculations, different model options for the spallation reaction and evaporation were used, as discussed below. By using the additional codes ORIHET3 [Atchison, 2001] and FP-FISPACT [Petrovich, 2001] the cumulative production rates were calculated.

As an example, in Figure 5.4.5 the calculated build-up of $^{127}$Cs as a function of the time after start of irradiation is shown. This isotope decays to $^{127}$Xe with a half-life of 6.25 h, thus contributing to the production of this isotope. In this case after about one day an equilibrium condition is reached, where the amount of $^{127}$Cs is constant.

**Figure 5.4.5. Calculated build-up of $^{127}$Cs after start of irradiation.**
*In this case equilibrium conditions are reached after about two days.*

![Graph showing build-up of $^{127}$Cs](image)

Measured isotopes

Collection measurements were performed for a number of isotopes. These include the release of He, Ne, Ar, Br, Kr, I, Xe, Hg, Po, and At radioisotopes.

During the first measurement run more attention was concentrated on those isotopes which are critical for the operation of an ADS target.

Offline $\gamma$ spectroscopy can be applied if the half-life of the isotope is longer than 10-15 minutes (the time it takes to get the sample to the germanium detector and begin the analysis with the acquisition program). Theoretically there is no upper limit in half-life, but to get good statistics one should choose isotopes with half-life less than some days or weeks, depending on the activity of the isotope.

### 5.4.1.5 First results

**Mercury**

Production of mercury isotopes is important as they are expected to contribute a significant part of the total radiotoxicity during operation of an LBE target.

Figure 5.4.6 presents the measured cumulative production rates for radioactive Hg isotopes. Longer-lived Hg isotopes are expected to be completely released at a temperature of 600°C. The ionisation efficiency was not measured for Hg, as it was only measured for noble gases. As discussed above, an efficiency of a factor 1.5 higher than the measured Xe efficiency of 3.7% was assumed.
The measured values are in line with expected cumulative production rates calculated using FLUKA and MCNPX. The two codes were coupled with the evolution codes ORIHET3 and SP-FISPACT, respectively. In the case of MCNPX, results are shown here with two different model combinations for the intranuclear cascade and evaporation models. The circles represent results from using the Bertini intranuclear cascade model with the Dresner evaporation code. The diamonds are obtained using the recently implemented INCL4/ABLA [Boudard, 2002] model combination. The trend observed in the data as a function of atomic mass is reasonably well reproduced by the three calculations. One should note that for $^{193}\text{Hg}$, $^{195}\text{Hg}$ and $^{197}\text{Hg}$, there are isomeric states of 11.1 h, 40 h and 23.8 h half-lives, respectively. For these three isotopes, equilibrium was not achieved between formation and decay of the respective isomeric states, and the data are not corrected for this effect. Overall these results confirm the expected production rates of Hg isotopes in a thick LBE target.

In Figure 5.4.7 a comprehensive display of the experimental results for Hg isotopes obtained with the three techniques with the LBE target is shown. Data refer to measurement with the target at 400°C, with the exception of the collection data which were taken at 600°C. However, it is apparent from the figure that at the two temperatures the released fraction of long-lived isotopes is very similar.

Figure 5.4.7. Measured production rates for Hg isotopes from the Faraday cup (triangles), $\gamma$ spectroscopy from collection data (squares), and $\beta$ detection from the tape station (circles)
Xenon and iodine

Results for Xe isotopes, also measured with the LBE target at T = 600°C, are shown in Figure 5.4.8. In this case there is a clear disagreement between the values calculated with MCNPX with Bertini/Dresner, and the results from the other two calculations. The data, with an ionisation efficiency of 3.7% for Xe isotopes seem to favour the other two calculation results, thus confirming recent experimental findings [Enqvist, 2001].

Figure 5.4.8. Same as Figure 5.4.6 but for Xe isotopes

While production of Hg isotopes from a Pb/Bi target is due to direct spallation, the Xe and I isotopes are the results from a later stage of the spallation process, the fission of highly-excited spallation fragments, or as a two-step process due to neutron-induced fission from high-energy spallation neutrons. Thus the evaporation models, the Dresner and ABLA, are probably most responsible for the differences observed in the calculations.

Similar results as for Xe are obtained for the iodine isotopes. However, iodine is not completely released and observed production rates at 600°C are a factor 10 lower than the calculated FLUKA values.

Polonium and astatine

In an LBE target the build-up of Po is a very important. 210Po is the isotope with the highest radiotoxicity among the volatile elements.

There are a number of possible reactions that can lead to astatine production. The dominating reaction is probably 209Bi (p, $\pi^-$ xn) 210$^-$ xAt.

The calculated production rates of Po isotopes are of the order of 10$^{10}$ atoms/µC. In the experiment, very small amounts of Po and At were observed. It was thus important to determine whether the observed Po came from At decay or it was indeed a release. By comparing the measured 207Po production rates at different times with 207At concentrations, it was concluded that even these small observed quantities are due to the decay of At and not to Po release. This is in agreement with other data [Neuhausen, 2004] which show that little or no release of Po is expected at temperatures of 600°C.
Helium

Production of He is of particular interest since this element, together with hydrogen represent the volatile elements produced in larger quantities during operation of a spallation target. The production rate for $^4$He measured with the Faraday cup is about 0.33 atoms/p, with an uncertainty of about 30%. This value is in good agreement with calculations with MCNPX, which gives values of 0.4-0.8 atoms/p, depending on the model combination used.

Other isotopes

Of the other isotopes measured and analysed, no release of Br was observed, while very little amounts of Cd isotopes were detected.

5.4.1.6 Conclusions and outlook

The first analysis from the measurements of production rates of volatile elements from the irradiated LBE target gives results consistent with the expectations from Monte Carlo calculations. Overall, these preliminary results confirm the expected production rates in an ADS target.

5.4.2. Irradiation experiments

5.4.2.1 Pb and LBE irradiated in the STIP experiments using the Swiss Spallation Neutron Source (SINQ)

The Swiss Spallation Neutron Source (SINQ) is currently operated at 0.6 MW with a proton beam of 1.1 mA current with an energy of 550 MeV. The SINQ targets are composed of a matrix of lead (Pb) rods clad with AISI 316L tubes. The Pb rods are 9.8 mm in diameter and about 120 mm long. The cladding tubes are of 9.8 mm inner diameter and 10.8 mm outer diameter. With the end caps, the total length of a target rod is 136 mm. During irradiation the target rods are cooled by flowing heavy water. The beam has an approximately 2-D Gaussian distribution profile. The irradiation dose and temperature depends on the positions in the target.

The SINQ Target Irradiation Program (STIP) has been carried out to irradiate test specimens in SINQ targets since 1998. To date, three irradiation experiments were performed and a fourth experiment has been run in the present target but will not be reported here. In the second irradiation experiment, STIP-2, which was performed in 2000 and 2001, there were two rods containing test specimens in contact with LBE. For the post-irradiation examinations (PIE) of the STIP-2 specimens, the specimen rods and some selected normal target rods were transferred to the hot cells of PSI in 2003. In 2004, some LBE and Pb samples were obtained from one of the two LBE rods (R-B) and a normal target rod (R-Pb3) for PIE.

The Pb rod, designated R-Pb3, received the highest proton fluence in SINQ Target-4 where the STIP-2 experiment was performed. The maximum proton and neutron fluences received by this rod were $5.5 \times 10^{25}$ p/m$^2$ and $9 \times 10^{25}$ n/m$^2$. The maximum irradiation temperature was about 538 ± 30 K measured at the centre of the rod.

The maximum proton and neutron fluences of the LBE rod R-B were $4.7 \times 10^{25}$ p/m$^2$ and $9.7 \times 10^{25}$ n/m$^2$. The maximum irradiation temperature was about 633 ± 40 K. It is believed that most of LBE was melted during irradiation. However, due to test specimens inside the LBE, the LBE
should remain static. The rod was cut into four segments. Four small pieces of LBE were obtained from each segment after re-melting it in a hot cell at about 443 K. Due to the high activity of the small pieces, the γ-spectrometry and ICPMS analysis are expected to be done in 2006.

5.4.2.2 LBE irradiated in the LiSoR experiment

The LiSoR (Liquid metal – Solid metal Reaction) loop is a unique facility which was designed to investigate simultaneously the influence of flowing lead bismuth eutectic (LBE), static stress and irradiation by protons onto a specimen.

The loop with the test section was designed and constructed by Subatech, France; the liquid metal pump and flow meter was delivered from IPUL, Latvia; assembling, cabling, isolating and commissioning was performed at PSI, Switzerland. The LiSoR test facility installed in the IP1 bunker is connected to a beam line from the Philips PSI accelerator. The beam energy on the target was about 72 MeV maximum for the five irradiation experiments while different beam currents between 15 and 50 μA were chosen for each irradiation period.

The loop was fabricated of austenitic stainless steel 316L whereas in the test section ferritic steel T91 was used. The flow rate of the pump is up to 0.3 l/s, which corresponds to a flow velocity of about 1 m/s in the test section. The total amount of LBE in the melting vessel was about 18 l whereby approximately 15 l were filled into the loop for operation.

As of this date five LiSoR test sections have been irradiated. After each irradiation cycle the loop was drained and the irradiated LBE was collected in the storage tank together with the non-irradiated remaining 5 l. After a reasonable decay time the test section was disconnected from the loop and transported into a hot cell for dissembling and examination. LBE was never changed or refilled, i.e. most of LBE was irradiated during all the experiments except that remaining in the storage tank. The isotopes generated during irradiation are mostly short-lived nuclides with half-life times in the range days at most. Only the isotopes 207Bi (T_{1/2} = 32.2 y) and 208Po (T_{1/2} = 2.898 y) have relatively long half-life times. The other isotopes except 207Bi and 208Po formed during the irradiation experiments 1 to 4 decayed. The time between irradiation experiment no. 4 (ended after only 144 h of irradiation on 25 June 2003) and no. 5 (irradiation started on 21 April 2004) was nearly 10 months, enough time for decay of the short-lived nuclides.

The eutectic Pb-55.5Bi (44.8 wt.% Pb and 55.2 wt.% Bi) alloy which was used for filling LiSoR was supplied by Impag AG, Switzerland and contained a very low concentration of impurities: Ag 11.4, Fe 0.78, Ni 0.42, Sn 13.3, Cd 2.89, Al 0.3, Cu 9.8 and Zn 0.2 ppm respectively. During the commissioning phase (app. 2000 h of operation with LBE temperatures between 473 and 573 K without irradiation) and during the five irradiation periods the level of impurities should have increased due to corrosion products (dissolving of steel elements) and formation of stable decay products.

The irradiated LBE after LiSoR 2 experiment was analysed with high-resolution α-spectroscopy on chemically separated solutions [Glasbrenner, 2005]. Additionally, calculations were made in order to compare them with the experimental results. In Table 5.4.1 the calculated values are compared with the experimental ones. The analysis was carried out about half a year after the irradiation was completed. Thus only Po isotopes could be analysed due to their relatively long half-life time. Calculations taking the correct beam parameters into account revealed the generation of the Po isotopes 202, 203, 204, 205 and 207. It is believed that these isotopes were present during and directly after irradiation but due to their short half-life times they were already decayed when the analysis was started. A comparison of the calculated and the experimental activities achieved for the Po isotopes 206 and 208 shows a good
Table 5.4.1. Values of Po isotopes revealed by neutronic calculation in comparison with experimental data

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Bq/calc.</th>
<th>Bq/g calc</th>
<th>Bq/g exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{202}$Po</td>
<td>$3.1 \times 10^7$</td>
<td>$1.6 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>$^{203}$Po</td>
<td>$2.3 \times 10^{11}$</td>
<td>$1.2 \times 10^9$</td>
<td></td>
</tr>
<tr>
<td>$^{204}$Po</td>
<td>$9.9 \times 10^{11}$</td>
<td>$5.3 \times 10^9$</td>
<td></td>
</tr>
<tr>
<td>$^{205}$Po</td>
<td>$1.1 \times 10^{12}$</td>
<td>$5.9 \times 10^9$</td>
<td></td>
</tr>
<tr>
<td>$^{206}$Po</td>
<td>$9.1 \times 10^{10}$</td>
<td>$4.8 \times 10^8$</td>
<td>$9.95 \times 10^5$</td>
</tr>
<tr>
<td>$^{207}$Po</td>
<td>$7.9 \times 10^{11}$</td>
<td>$4.2 \times 10^9$</td>
<td></td>
</tr>
<tr>
<td>$^{208}$Po</td>
<td>$5.9 \times 10^{9}$</td>
<td>$3.1 \times 10^3$</td>
<td>$4.8 \times 10^4$</td>
</tr>
<tr>
<td>$^{210}$Po</td>
<td>$2.0 \times 10^6$</td>
<td>$11$</td>
<td>$150$</td>
</tr>
</tbody>
</table>

Consistence of the values, whereas the estimation of the $^{210}$Po activity is too low. The generation of the $^{210}$Po isotope requires thermal neutrons and the FLUKA code has only included reactions with fast neutrons. It is definitely possible that during the irradiation a small amount of thermal neutrons are generated which are responsible for the formation of $^{210}$Po. For future calculations the FLUKA code has to be modified or another tool has to be used for performing these calculations.

During dissembling of LiSoR test section No. 5 samples of irradiated LBE were taken out from different positions. All irradiated LBE samples were examined by the following techniques:

- $\gamma$-spectrometry of solid materials but also of dissolved LBE samples to detect nuclides decaying by gamma irradiation;
- $\alpha$-spectrometry on special processed LBE samples to analyse the different Po isotopes;
- ICP-MS on dissolved LBE probes to analyse all elements present in the different LBE samples.

In parallel to the analytical examinations calculations will be carried out using the FLUKA Monte Carlo code to compare the different analytical results with the calculations.
REFERENCES


Perret, Ch. (2002), Sicherheitsbericht zum MEGAPIE-Experiment an einem Target mit flüssigem Blei-Bismut-Eutektikum in der Neutronenquelle SINQ des PSI-West, PSI, June 2002.


Zanini, L., M. Vatre (2005), Monte Carlo Calculations of Activation of the MEGAPIE Target, PSI report TM-34-05-5.

Chapter 6
COMPATIBILITY OF STRUCTURAL MATERIALS WITH LBE AND Pb:
STANDARDISATION OF DATA, CORROSION MECHANISM AND RATE*

6.1 Introduction
The reasons for choosing lead (Pb) or lead-bismuth eutectic (LBE) as coolant and spallation target of accelerator-driven systems (ADS) have been mentioned in the introduction to this handbook. However, Pb and LBE show high aggressiveness for conventional structural materials. An understanding and mitigation of corrosion and degradation of mechanical properties of structural materials in Pb and LBE are essential issues for the demonstration of technical feasibility of critical and subcritical systems. In addition, the availability of technologies that allow for safe operation of lead alloy facilities is also essential.

Chapter 6 focuses on the compatibility of structural materials, mainly stainless steels, with lead-bismuth eutectic and lead, dealing with the corrosion mechanism and rate. First, the fundamentals of corrosion and protection methodologies by \textit{in situ} oxide layer formation are discussed. Second, a critical review of the existing data on corrosion of structural steels in LBE and Pb is presented, with the main conclusions obtained from these data. Finally, recommendations on corrosion tests procedure are proposed.

6.2 Fundamentals

6.2.1 Corrosion
Structural materials exposed to liquid metals can undergo corrosion by: (1) direct dissolution of the solid metal in the liquid metal by a surface reaction involving atoms from the solid and the liquid metals or impurities present in the liquid metal, and (2) by intergranular attack. In the dissolution process or leaching, one component of the alloy is preferentially dissolved, as in the case of nickel that is leached from stainless steels by lead and lead bismuth eutectic [Sheir, 1994]. In the dissolution process two stages can be identified. The first stage involves “cleavage” of the bonds between atoms in the solid metal and the formation of new bonds with atoms of liquid metal or its impurities, in the boundary layer. Once this occurs, the dissolved atoms diffuse through the boundary layer into the liquid metal.

The driving force for corrosion is the difference between the chemical activities of the solute metals between the surface and the LBE. The chemical activity is dependent on the solubility and the chemical activity of the element in the solid phase, which is less than unity for all components in stainless steels. Therefore, the maximum concentration of the solute metal at the boundary of the two phases is determined by its chemical activity in the solid phase.

* Chapter lead: Laura Soler Crespo (CIEMAT, Spain). For additional contributors, please see the List of Contributors included at the end of this work.
The overall rate-controlling step is the diffusion through the boundary film of solute atoms into the flowing stream. Under static conditions at constant temperature:

\[ a_t = a_o \left[ 1 - \exp\left(-\alpha \frac{St}{V}\right) \right] \]  

(6.1)

where \( a_t \) is the concentration of solute after time \( t \), \( a_o \) is the saturation concentration of solute in equilibrium with the solid state; \( S \) is the surface area of solid exposed to liquid of volume \( V \), \( \alpha = \alpha_o \exp[-\Delta E/RT] \), where \( E \) is the activation energy for dissolution.

Under isothermal and stagnant conditions, the laminar boundary is not as well defined as in a flowing system and the diffusion path cannot be defined.

The corrosion rate decreases with the time following an exponential law and the dissolution process stops when the concentration of the elements in the liquid metal reaches the saturation value. Therefore, corrosion by the direct dissolution process can be minimised by selecting a containment material whose elements have low solubility in the liquid metal of interest or by saturating the liquid metal before actual exposure. Measurements of weight changes as a function of time for a fixed \( a_o-a_i \) yield the kinetic information necessary for determination of the rate-controlling mechanism.

Under flowing conditions:

\[ \frac{da_t}{dt} = K \left( \frac{S}{V} \right) (a_o-a_i) \]  

(6.2)

where \( K \) is a rate constant, which is usually related to the diffusion rate through the boundary layer. In a flowing recirculating system, the precipitation process in the cold leg or heat removal part of the circuit often controls the steady-state concentration of the solute. The material dissolved at the highest temperature will precipitate at the lowest temperature until a steady state is reached. The corrosion rate is a function of both the maximum and minimum temperature in the circuit and the corrosion rate at the highest temperature can be reduced by increasing the minimum temperature or by reducing the maximum temperature [Weeks, 1997]. This type of corrosion is termed thermal gradient mass transfer. It can be illustrated by circulating a corrosive metal such as bismuth round a thermal convection loop of the type shown in Figure 6.2.1 [Weeks, 1956]. Mass is transferred from the hot zone to the cold zone and, after a period of time, the plugging of the loop may occur. This type of corrosion does not decrease with time, contrary to the observed in isothermal conditions. If the liquid metal is flowing at high velocity, the structural materials could be also subject to erosion-corrosion. The erosion can be classified to the widely damaged surface along the flow as if fluid carries out the surface material by a strong dynamic pressure and the pitting type erosion where material is deeply lost from narrow surfaces [Kondo, 2005].

Mass transfer can also occur under isothermal conditions where concentration gradients exist. The dissolved elements from one alloy can be transported by the liquid metal and precipitate or dissolve in another alloy, forming metal solid solutions or intermetallic compounds. In some cases selective dissolution can be used to advantage by "masking" one region of the system by material dissolved from another region of the system. Masking can be described as the lowering of element loss from a downstream region because a region rich in these elements is located upstream. For example, the removal of nickel from nickel containing alloys is an important factor determining the corrosion rate of these materials. If a high nickel source is placed upstream in an isothermal zone, the nickel removal rate from a region downstream could be reduced due to the higher Ni content in the coolant adjacent to this region which reduces the activity difference between the surface and the bulk.
Intergranular attack occurs because the atoms at the grain boundary have a higher potential energy than the atoms inside the grains. Therefore, the activation energy of the grain boundary atoms for dissolution is lower and the probability of their transition to the melt and, hence, the dissolution rate, higher. If the concentration of higher solubility elements increases in the grain boundaries, the dissolution rate may increase due to the preferential dissolution of these elements [Gerasimov, 1983].

A general discussion of the different types of corrosion in liquid metals and of the influence of several variables (temperature, temperature gradient, ratio metal solid area to liquid metal volume, velocity and others) can be found in [Staudhammer, 1992], [Bagnall, 1995].

6.2.2 Oxidation

Oxygen concentration in liquid lead alloys is a key parameter for the corrosion of structural materials. Several authors have correlated decreased dissolution resistance in Pb and LBE with low oxygen concentration. Gorynin, et al. [Gorynin, 1999] determined the influence of oxygen concentration on the corrosion/oxidation process of two austenitic stainless steels (18Cr-11Ni-3Mo commercial steel, and 15Cr-11Ni-3Si-MoNb experimental steel alloyed with 3% Si) in experiments performed in flowing lead at 550°C, for 3000 hours. For oxygen concentrations between \(10^{-8}\) and \(10^{-10}\) wt.%, corrosion by dissolution occurs whereas for concentrations higher than \(10^{-7}\)-\(10^{-6}\) wt.% oxidation of steels takes place (Figure 6.2.2). The corrosion observed for low oxygen concentrations (\(10^{-8}\)-\(10^{-10}\) wt.%) begins with the formation of pits on the material surface. During exposure, the pits grow and merge into a porous corrosion layer, whose thickness grows linearly with time. Figure 6.2.2 shows the effect of oxygen concentration on corrosion resistance for stainless steels. There is a minimum in material loss associated with the formation of a protective oxide film.
With an adequate control of the oxygen concentration in the liquid metal, the formation of oxide films on the surface of the structural materials occurs, limiting further dissolution. For the optimum effectiveness, the oxygen concentration in the liquid metal has to be adequate to passivate the material but not sufficiently high to promote the precipitation of lead oxide. For Fe containing alloys, such as structural steels, the minimum oxygen concentration is defined by the magnetite ($\text{Fe}_3\text{O}_4$) decomposition potential, considering this oxide the less stable of the ones that can be formed on structural steels. The maximum value is fixed by the precipitation of lead oxide. After the formation of oxide films, the dissolution of the structural materials becomes negligible due to the low diffusion rate of the alloying elements of steels in the oxides. The ideal protective oxide layer should be pore-free, crack-free, stress-free at operating temperatures, and resistant to spalling or damage during cooling or heating [Stott, 1987]. In addition, the oxygen and metal ions must have low diffusion coefficients through the scale and the recession rate of the original surface must be low enough during the desired service life [Kofstad, 1987]. For a practical lead-alloy coolant system, it is nearly impossible to set up such an ideal protective layer. However, it is possible to optimise the self-healing layer by controlling the oxygen concentration in the liquid lead/lead-bismuth, and changing steel compositions and operating conditions. This optimisation has finally the scope to minimise the corrosion-dissolution process and the corrosion-oxidation process.

Data on the influence of other elements on the corrosion resistance of structural steels in liquid lead alloys have been provided by Gorynin, et al. [Gorynin, 1998], [Gorynin, 1999]. For instance, Si increases the corrosion resistance of several steels in flowing lead-bismuth with oxygen concentrations lower than $10^{-7}$ wt.%, at 460°C, whereas for low oxygen concentrations ($10^{-8}$-$10^{-10}$ wt.%) in lead at 550°C the Si influence is not significant [Gorynin, 1999]. The effect of other alloying elements such as Cr, Ti, Nb, Si and Al on low alloy steels corrosion in flowing lead-bismuth at 600°C was studied by the same authors. A significant decrease of the dissolution was observed for concentrations of Si and Al around 2% whereas for the rest of the elements, concentrations higher than 3% seem to be needed to obtain similar effects. In general, in reducing environments, in which the formation of protective oxide layers is not possible, steels with lower chromium concentration show lower dissolution rate. Austenitic steels suffer accelerated attack in lead and lead-bismuth due to the high nickel solubility. Yachmeniov has recommended limiting temperatures for the application of non-protected stainless steels to around 450°C for ferritic-martensitic steels and 400°C for austenitic steels [Yachmeniov, 1998].
The oxide layer structure of steel in liquid lead-alloys with oxygen control, in principle, depends on the steel composition, temperature and hydraulic factors. Generally, there are two possible oxide structures for martensitic steels according to the available experimental results [Balbaud-Celerier, 2003]:

- For temperatures below 550°C, it is composed of an external magnetite layer, Fe₃O₄ and a compact internal Fe-Cr spinel oxide layer. In some cases, the external magnetite layer is not observed. Penetrations of lead are sometimes observed in the outer layer. The duplex layer can protect steels from dissolution.
- For temperature above 550°C, an internal oxidation zone with oxide precipitates along the grain boundaries is observed below the Fe-Cr spinel layer.

Austenitic steels generally contain more Cr and Ni than martensitic steels. The oxide layer formed on austenitic steels has the following possible structures [Zhang, 2004]:

- For temperature below 500°C, the oxide layer is very thin and is composed of the single-layer Fe-Cr spinel, which can prevent direct dissolution.
- For temperature around 550°C, the oxide layer can have either duplex- or single-layer structure, depending on the surface and operating conditions. The duplex-layer oxide can prevent steel component dissolution, while heavy dissolution is observed when the single-layer oxide forms.
- For temperature above 550°C, heavy dissolution occurs.

For a static case, if the liquid is saturated with the steel components, no steel components can be further released to the solution. The oxide structures are then similar to that in gaseous environment. For other cases with scale removal, the possible oxide structures of stainless steels (martensitic or austenitic steels) in liquid lead-alloys with oxygen control are shown in Figure 6.2.3.

Figure 6.2.3. Possible oxide structures of stainless steels in liquid lead alloys with oxygen control [Chang, 1990]
The oxide scale can be removed due to mass transfer corrosion. In practice, erosion can occur at locations where the flow changes its direction suddenly, such as a bend, an expansion, etc. The liquid particles can attack the protective layer and the high shear stress may strip the layer away. Such attacks can enhance the oxidation mechanism and lead to a higher degradation rate of the surface. Chang, et al. [Chang, 1990] classified the erosion-oxidation phenomena into four categories: 1) erosion of oxide only; 2) erosion enhanced oxidation; 3) oxidation affected erosion; 4) erosion of metal only. Rishel, et al. [Rishel, 1991] proposed that there are three types in erosion enhanced oxidation range (Figure 6.2.4).

Figure 6.2.4. Erosion-oxidation interaction regimes [Rishel, 1991]

The active oxygen control technique is based on the fact that lead and bismuth are chemically less active than the major alloying elements of structural steels (Ni, Fe, Cr). The molar free energy of formation of the oxides of Ni, Fe and Cr is lower than that of lead and bismuth oxides, as can be seen in the Ellingham diagram in Figure 6.2.5.

To prevent PbO precipitation and to support Fe$_3$O$_4$ formation, the following conditions must be established:

$$2 \Delta G^o_{\text{PbO}} > RT \ln p_{O_2} > 0.5 \Delta G^o_{\text{Fe}_3\text{O}_4}$$  \hspace{1cm} (6.3)

where $\Delta G^o$ is the Gibbs energy for formation of oxides, $p_{O_2}$ is the oxygen partial pressure, R is the gas constant and T is the absolute temperature.
The reaction resulting in the formation/dissolution of magnetite in liquid lead or lead-bismuth can be expressed as:

\[ 4 \text{O} + 3 \text{Fe} \rightleftharpoons \text{Fe}_3\text{O}_4 \]  
(6.4)

with the equilibrium constant:

\[ K_e = a[\text{Fe}_3\text{O}_4]/a^4_\text{O} \times a^3_{\text{Fe}} \]  
(6.5)

where Fe, O and Fe$_3$O$_4$ are dissolved in the liquid metal, and $a$ is the thermodynamic activity of the substances present in solution.

If $a[\text{Fe}_3\text{O}_4] = 1 \Rightarrow a^4_\text{O} \times a^3_{\text{Fe}} = \text{constant at constant } T$  
(6.6)

For example, at 400°C and for $a_{\text{Fe}} = 1$, the equilibrium oxygen activity is $1 \times 10^{-6}$ corresponding to an oxygen concentration of $1 \times 10^{-10}$ wt.%. If $a_{\text{Fe}} < 1$, the oxygen activity will be higher.

The equilibrium oxygen activity as a function of the temperature for constant concentrations of oxygen and iron in lead-bismuth eutectic can be seen in Figure 6.2.6 [Li, 2002]. Steel corrosion via dissolution occurs below a minimum value of activity, $a_{\text{min}}$, for which Fe$_3$O$_4$ is unstable, whereas coolant contamination by lead oxide formation takes place in the region above $a = 1$. Setting the maximum and minimum values of temperature of the liquid metal in a loop and assuming the oxygen concentration at minimum temperature equal to the saturation value, the permissible range of oxygen activity values can be determined.

According to Yachmenyov, et al. [Yachmenyov, 1998], an oxygen concentration $C_i > C_{\text{min}}$ will be necessary to form a protective film with the structure of spinel. $C_{\text{min}}$ is the minimum concentration of
oxygen dissolved in the liquid LBE to maintain passivity of the materials. \( C_{\text{min}} \) must be higher than the equilibrium oxygen concentration for the magnetite existence, \( C_T^{\text{min}} \), when \( a_{\text{Fe}} = 1 \). At \( C_i < C_{\text{min}} \), substantial corrosion of the steels occurs. The morphology of corrosion depends on the value of \( C = C_{\text{min}} - C_i \), but also on the steel composition, temperature and time. In practice, the corrosion process is kinetically controlled [Shamatko, 2000], and the corrosion of steels occurs for values of \( C_T^{\text{min}} < C_i < C_{\text{min}} \) for which the process of steel dissolution prevails over that of steel oxidation.

During the system operation, different processes can modify the oxygen activity to values out of the permissible range. Impurities present in the coolant with oxides more stable than the iron oxide can decrease the oxygen concentration down to values lower than the needed for the formation of magnetite. Transmutation elements generated by the proton beam in the coolant can disturb the chemical equilibrium in the loop. Reduction-oxidation reactions can occur with the formation of non-soluble oxides, and with the reduction of the oxide protective layers [Gromov, 1998]. On the contrary, air in-leaks can increase the oxygen activity.

To control the oxygen activity in flowing liquid metal systems, several procedures have been developed in the past by Russian researchers [Efanov, 2001] and, at present, they are being revisited in different laboratories in Europe and USA [Knebel, 1999]. A detailed description of this procedure is given in Chapter 4 of this handbook, Section 4.3, entitled Oxygen control in lead and LBE systems. For oxygen control monitoring on line, electrochemical sensors for oxygen activity measurements were developed by Russian researchers and, recently, reference electrodes of \( \text{In/In}_2\text{O}_3 \), \( \text{Bi/Bi}_2\text{O}_3 \) and others are being developed and tested in several labs under different conditions. A detailed description of these sensors is given in Chapter 4, Section 4.4, On-line electrochemical oxygen sensors.

6.3 Summary and critical review of the data

The sources for the existing data on corrosion in LBE/Pb are the scientific literature on LBE and Pb technology, the TECLA European Project reports and international workshops on this subject. Corrosion tests of a wide variety of materials under wide ranging conditions have been carried out in both stagnant and flowing LBE/Pb. The steels tested include Fe-Cr steels, with chromium contents from 1.2 to 16.24 wt.% (SCM420, P22, F82H, STBA28, T91, NF616, ODS-M, Eurofer 97, STBA26,
Optifer Ivc, EM10, Manet II, 56T5, ODS, EP823, HT9, HCM12A, HCM12, 410ss, T410, 430ss). The composition of these steels is shown in Table 6.3.1. Austenitic steels tested include D9, 14Cr-16Ni-2Mo, 1.4970, 316L, 304L, and 1.4984. The composition of these materials are shown in Table 6.3.2. The test temperatures range from 300 to 650°C, times from 100 to 10000 hours and oxygen concentration in LBE/Pb from 10^{-12} wt.% to saturation. Tables 6.3.3-6.3.8 collect all the data available at each experimental condition. These tables are divided into: 1) Fe-Cr steels in stagnant LBE; 2) austenitic steels in stagnant LBE; 3) Fe-Cr steels in flowing LBE; 4) austenitic steels in flowing LBE; 5) steels in stagnant Pb; 6) steels in flowing Pb. Data included in the tables are the material, temperature, time, oxygen control system, oxygen concentration, exposed steel surface/LBE or Pb volume ratio and oxide layer thickness/dissolution depth or weight change measurement, and the reference. The general qualitative corrosion behaviour (oxidation or dissolution) is also included, following the indications of the authors. Some observations are also included concerning the morphology of the corroded steel surface. At least four different cases have been detected: 1) clear dissolution; 2) coexistence of relatively thin oxide layers with dissolution zones; 3) thick oxide layers, that, in some areas spall and in others allow the penetration of LBE; 4) clear oxidation. Of course, the two intermediate cases are difficult to interpret and a clear distinction is often not possible and subject to the author’s interpretation. In Cases 1 and 2, dissolution is indicated and in Cases 3 and 4, oxidation. In the case of flowing conditions, the name of device (described in Chapter 12) and the fluid flow rate is included.

These tables collect all the data available. However, it is difficult to establish comparisons due to the wide range of experimental conditions used and the lack of standardisation of the corrosion tests. Not all the collected papers provided all the experimental conditions. In the cases in which oxygen contents are not reported, data have been considered invalid. This is the case of references [Soler, 2001], [Gnecco, 2004]. Other data have been included although the results were surprising, as it is the case of references [Benamati, 2002], [Long Bin, 2003], [Kurata, 2005], in which Manet martensitic steel and JPCA and 316ss austenitic steels tested at 550°C for 3000 hours present dissolution in oxygen saturated LBE. This data are marked with a star in Figures 6.3.1-6.3.10.

A first screening of the data was made using only the qualitative corrosion behaviour (oxidation or dissolution), eliminating the invalid data and using only the data of the longest duration tests, keeping the rest of conditions equal. With these data, a semi-quantitative analysis was made, representing the general corrosion behaviour in a graphic of temperature versus oxygen concentration. These graphics are shown in Figures 6.3.1-6.3.10. Specific graphics for the martensitic steel T91 and the austenitic steel AISI 316L are included, since these steels have been chosen as reference materials for further research in many laboratories.

In these graphics, the line of formation of magnetite and the saturation line (PbO formation) are indicated. Even though these graphics are semi quantitative (some points corresponds at different materials and times and only a qualitative indication of the corrosion behaviour is given), they are very useful to determine the temperature and oxygen concentration areas for which the protection by oxide layer formation is feasible. In all the cases, below the magnetite formation line dissolution takes place. In general, under stagnant LBE, at 600°C dissolution occurs and between 500 and 550°C there are dissolution or oxidation depending on the material. For austenitic steels, the general behaviour is similar, but the steels suffer stronger dissolution under reductive conditions and they present thinner oxide layers under oxidant atmospheres. In flowing conditions, there are less data, with a line around 10^{-6} wt.% oxygen concentration below which dissolution takes place. For T91 and 316L steels under stagnant conditions, there is dissolution at 600°C and below 10^{-6} wt.% oxygen concentration. Under flowing conditions, there are few data and the maximum temperature tested is 470°C, and it is not possible to get any conclusions. For steels tested in lead, there are very few data both under stagnant and flowing conditions.
Figure 6.3.1. Fe-Cr steels in stagnant LBE

$T_e = 300-650^\circ C$
$t = 100-5000 \text{ h}$
$[O] = \text{From } 10^{-12} \text{ wt.}\% \text{ to saturation}$

Figure 6.3.2. Fe-Cr-Ni steels in stagnant LBE

$T_e = 300-600^\circ C$
$t = 100-10000 \text{ h}$
$[O] = \text{From } 10^{-10} \text{ wt.}\% \text{ to saturation}$
Figure 6.3.3. Fe-Cr steels in flowing LBE

$T_e = 300-600\,^\circ C$

$t = 340-7200\, h$

$[O] = \text{From } 10^{-9} \text{ to } 10^{-5}\text{wt.}\%$

---

Figure 6.3.4. Fe-Cr-Ni steels in flowing LBE

$T_e = 400-600\,^\circ C$

$t = 700-7200\, h$

$[O] = 10^{-9}-10^{-5}\text{wt.}\%$
Figure 6.3.5. T91 steel in stagnant LBE

T = 350-600°C

\[ t = 100-3000 \text{ h} \]

\[ [O] = 10^{-12} \text{ wt.\%} - \text{saturation} \]

Figure 6.3.6. T91 steel in flowing LBE

\[ T = 300-470°C \]

\[ t = 1116-4500 \text{ h} \]

\[ [O] = 10^{-9}-10^{-5} \text{ wt.\%} \]
Figure 6.3.7. AISI 316L steel in stagnant LBE

$T^e = 300-600^\circ$C

$t = 100-10000$ h

$[O] = 10^{-10}$ wt.% – saturation

Figure 6.3.8. AISI 316L steel in flowing LBE

$T^e = 400-600^\circ$C

$t = 959-7200$ h

$[O] = 10^{-9}-10^{-5}$ wt.%
Figure 6.3.9. Steels in stagnant Pb

$T^e = 464-550^\circ C$

$t = 700-3700h$

$[O] = 8 \times 10^{-6} \text{ wt.\%} - \text{satisfaction}$

Figure 6.3.10. Steels in flowing Pb

$T^e = 400-550^\circ C$

$t = 1027-3027h$

$[O] = 3-4 \times 10^{-5} \text{ wt.\%}$
6.4 Conclusions and further data needed

For tests conducted both in stagnant and in dynamic (flowing) LBE/Pb within the oxygen control band, most Fe-Cr and Fe-Cr-Ni steels form oxides that are protective below temperatures in the range 500-550°C, specially for an oxygen concentration above $10^{-6}$ wt.% for short- to medium-term applications.

Austenitic steels show thinner oxide layers. For oxygen concentrations lower than $10^{-6}$ wt.%, dissolution takes place in most of the steels, especially austenitic steels, due to the high solubility of nickel in LBE/Pb. For tests temperatures higher than 550°C, the formation and protectiveness of oxides is uncertain, and protection usually fails due to dissolution for long times.

Similar compositions of the oxide layers formed in Pb-Bi and Pb experiments have been described by several authors. In general, the steels show a double oxide layer formed by an outer layer with a composition comparable to that of magnetite and an inner layer where Cr content is higher than in the material bulk. The composition of this inner layer correspond to Fe(Fe$_{1-x}$Cr$_x$)$_2$O$_4$.

Further data needed

As was pointed out in this chapter, the existing data base for the corrosion of materials in LBE/Pb is very sparse in some areas. Additionally, the actual environment that existed during many of the reported test results is open to question. For example, it would seem to be improbable that dissolution would be the dominant corrosion mechanism for a stainless steel exposed at oxygen potentials near the PbO potential. Lastly, the state of the art of oxygen potential measurement is rapidly improving but for many of the reported test data, poorly measured. Thus, it is expected that much more data will be needed in the future in order to assure adequate system design. To this end, additional data is required in the following areas:

- Long-term tests (15000 hours) in dynamic conditions to confirm the actual oxygen-temperature areas, especially for T91 and 316L steels to support the design of future systems in which these steels have been chosen as reference.
- Tests in stagnant and flowing lead to expand the database in Pb at high temperature
- Influence of several parameters (surface state of steels, stresses, welding, etc.) on the corrosion response of steels to improve the knowledge about the dissolution/oxidation process and to support models and mechanisms.
- For high temperature systems (above 550°C), development and testing of advanced materials will be also needed.

6.5 Recommendations on corrosion tests procedure (standardisation)

Analysis of the available data indicates that a wide range of experimental conditions have been tested: temperatures from 300 to 650°C, times from 100 to 10000 hours and oxygen concentration in LBE/Pb from $10^{-12}$ wt.% to saturation.

Thirteen Fe-Cr steels and eleven Ni alloys have been tested. However, there are not enough data for each condition and, in some cases, not all the experimental conditions are reported. The result has been that much of the data cannot be properly interpreted. This indicates that it is necessary a more systematic work to be able to standardise the test procedures, but it is possible to give some general recommendations.
The approach to testing in LBE or Pb involves design and placement of samples, design of test system, the control and monitoring of tests conditions and the measurement and evaluation of corrosion damage. The general recommendations that follow are based on [Bagnall, 1995].

In order to assure valid results, tests should be well documented, and the following systematic parameters should be reported.

6.5.1 **Pre-test preparation**

6.5.1.1 **Liquid metal: LBE and Pb**

- Impurity analysis of the LBE or Pb should be made before and after each test.
- Total mass of LBE/Pb.

6.5.1.2 **Material**

- Composition.
- Thermo-mechanical treatment.
- Type of product.
- Mechanical and microstructure characteristics (hardness, etc.).
- Shape.
- Length.
- Thickness.
- Mass.
- Surface preparation: as mechanised, ground, electrolytic polished, etc. The test specimens should start its period of exposure with relatively smooth and readily reproducible surface conditions. The surface finishing should not introduce metallurgical changes in the surface.

The samples should be correctly identified using a technique that will not be destroyed during the test.

6.5.2 **Test conditions**

The compatibility of materials with heavy liquid metals can be studied using static, thermal convection and forced convection conditions. A detailed description of the typical systems is included in Chapter 12.

6.5.2.1 **Static (no flow) tests**

In isothermal devices for tests in stagnant LBE/Pb, the container can serve as test specimen, or the test specimen can be incorporated. In any case, the container and test specimen should be either of the same composition or, better, the container should be inert to corrosion in liquid metals. Relative surface areas of different metals and surface/liquid metal volume ratios are important points to consider.
when designing small scale tests to examine corrosion trends. The liquid metal volume to exposed area metal ratio should be high enough to avoid saturation of main steel elements in the liquid metal. In general, materials with large compositional differences should not be exposed together to determine relative corrosion behaviour.

Temperature should be uniform in the liquid metal contained in the device. The oxygen content in LBE or Pb should be homogenised and known during the test period.

Stagnant tests are very useful to give a first screening of experimental conditions and contribute to the establishment of a corrosion mechanism in LBE/Pb. However, in isothermal conditions, the rate of dissolution reaction would decrease with time as the concentration of the main steel elements dissolved in the liquid metal increases. After a period of time, the actual elemental concentration becomes equal to the solubility and the dissolution rate is zero.

6.5.2.2 Dynamic tests

The simplest non-isothermal flowing system where processes associated with dissolution and deposition occur is one in which flow is induced by thermal convection. This is accomplished by heating one leg of a closed loop and cooling another leg. The flow rate is dependent on the height of the heated and cooled sections, on the temperature gradient and on the physical properties of the liquid. Thermal convection loops can be destructively examined after operation and specimens can be removed and replaced numerous times for cumulative periods without interruption of liquid metal flow. However, the utility of thermal convection loops is limited by the low flow velocities that can practically be achieved (maximum of about 60 mm/s), making extrapolations to the higher velocities in operating systems doubtful.

Higher flow velocities are obtained in forced convection loops where the liquid is pumped through the loop with an electromagnetic or mechanical pump. Test specimens of various materials are generally placed in the hot leg and the effect of the flowing liquid on the specimen is determined from changes in weight, dimensions, mechanical properties, and microstructure. Such an approach yields data on maximum corrosion rates as a function of temperature and liquid metal flow rate. The chemical balance between dissolution and deposition is strongly influenced by all materials (i.e. containment and tests specimens) exposed to the circulating LBE or Pb. The containment material has its own effect on test results in systems in which dissimilar metals or alloys are involved.

The parameters that should be taken into account during tests under flowing LBE or Pb are:

- **Materials.** Steel composition of the loop and test specimens must be analysed and reported. The test specimen distribution in the loop should always be given in detail when reporting corrosion results. Relative corrosion sources and sinks are of vital importance in the analysis of corrosion specimens.

- **Temperature.** Maximum and minimum temperature of the loop must be measured and reported during the loop operation. However, corrosion rate/temperature relationships are strongly influenced by system geometry. For this reason, loop geometry and temperature distribution along the loop should be also measured and reported during a test.

- **Flow rate.** In general, flow rate influences corrosion rate by LBE or Pb. If the liquid metal is flowing at high velocity, the structural materials could be also subject to erosion. It is necessary to measure and report the flow rate at several points of the loop, especially at the test sections.
- **Time.** Accurate kinetic measurements must be made over an extended time period for useful comparison and predictive analysis. The proposed exposure intervals are 2000, 5000, 10000 and 15000 hours. Accelerated corrosion takes place in the first hours of exposure, depending on the material and temperature, but 2000 hours seems a reasonable time to detect this period. After this initial period, a steady-state corrosion rate is usually attained. Accurate kinetic measurements must be made over an extended time period for useful comparisons and predictive analysis.

- **Oxygen concentration in LBE or Pb.** Corrosion inhibition is dependent on formation of protective surface films and control of oxygen in the liquid metal is essential for this process. The oxygen control system used to adjust and assure the required oxygen in the LBE or Pb – gas mixture, \( \text{H}_2/\text{H}_2\text{O} \) equilibrium or solid PbO – should be always reported. The knowledge of the oxygen concentration in the LBE or Pb is mandatory. This value, together with temperature, will give the valid area of operation.

### 6.5.3 Post-test analysis

The development of a common criteria to quantify LBE or Pb effects on materials is essential for comparison of results from different labs and to reach conclusions. In general, the corrosion damage and the oxidation observed is heterogeneous, with simultaneous existence of dissolution areas and oxidation protected areas. In these cases, weight change measurements alone could lead to erroneous interpretation. There is not a single method reliable for all the cases. For comparison, one should perform metallographic examination, weight change measurements and try to measure the remaining unaffected thickness of interior bulk.

- **Metallographic examination.** Cross-section of the tested steels without removal of the remaining LBE or Pb should be used for the analysis of the oxide layer formed on the surface or the morphology of dissolution and its depth. The oxide layer should be characterised focusing on the following parameters:
  - **Thickness.** It should be measured at several zones and give a medium value.
  - **Structure.** Indicate porosity, adherence, hardness, etc.
  - **Composition.** Indicate enrichment or depletion of the main steel elements.
  - **General aspect.** LBE/Pb penetration, spalling, etc. It is useful to attach a photograph.

All these items should be reported.

- **Weight change measurements.** For this method, the removal of solidified LBE or Pb from the test specimen without damaging the surface or destroying a layer or deposit is required. The methodology of cleaning – mercury or silicone baths at a certain temperature, etc. – must be reported. The use of mercury is not recommended since it is highly hazardous.
Table 6.3.1. Composition of Fe-Cr steels

<table>
<thead>
<tr>
<th>SCM</th>
<th>2,25Cr-1Mo</th>
<th>FR2H</th>
<th>STBA 28</th>
<th>T91</th>
<th>NF 616</th>
<th>ODS-M</th>
<th>Eurofer 97</th>
<th>STBA 26</th>
<th>Optifer 1Vc</th>
<th>EM10</th>
<th>56T5</th>
<th>12CR</th>
<th>ODS</th>
<th>EP823</th>
<th>HT9</th>
<th>HCM 12A</th>
<th>HCM 12</th>
<th>410ss</th>
<th>T410</th>
<th>430ss</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.010-11</td>
<td>0.10-</td>
<td>0.10</td>
<td>0.13</td>
<td>0.12</td>
<td>0.01</td>
<td>0.11</td>
<td>0.20</td>
<td>0.11</td>
<td>0.14</td>
<td>0.18</td>
<td>0.22</td>
<td>0.067</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>1.2</td>
<td>2.18-</td>
<td>7.70-7.75</td>
<td>8.41-8.6</td>
<td>8.26-8.63</td>
<td>8.8-9</td>
<td>8.85</td>
<td>9.05</td>
<td>10.3</td>
<td>10.54</td>
<td>11.72</td>
<td>10.97</td>
<td>12</td>
<td>12.5</td>
<td>16.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.02</td>
<td>0.015</td>
<td>0.06</td>
<td>0.01</td>
<td>0.022</td>
<td>0.04-0.2</td>
<td>0.68</td>
<td>0.33</td>
<td>0.75-0.89</td>
<td>0.59</td>
<td>0.12</td>
<td>0.34</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.2</td>
<td>0.92-</td>
<td>0.88-1</td>
<td>0.9-1</td>
<td>0.91-0.95</td>
<td>0.3-0.5</td>
<td>0.0015</td>
<td>0.97-1</td>
<td>0.61</td>
<td>0.34</td>
<td>0.7-0.73</td>
<td>1.11</td>
<td>0.3</td>
<td>1.1</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>1.94-2.10</td>
<td>&lt;0.01</td>
<td>1.8-1.9</td>
<td>1.94</td>
<td>1.07</td>
<td>1</td>
<td>0.005</td>
<td>1.76</td>
<td>1.99</td>
<td>0.64</td>
<td>1.9</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.44-0.55</td>
<td>0.01-</td>
<td>0.30-</td>
<td>0.31-</td>
<td>0.30-0.43</td>
<td>0.3</td>
<td>&lt;0.005</td>
<td>0.20-0.43</td>
<td>0.37-0.44</td>
<td>0.22</td>
<td>0.27</td>
<td>1.21</td>
<td>0.3</td>
<td>0.3</td>
<td>0.31</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.2</td>
<td>0.34</td>
<td>0.1-0.23</td>
<td>0.3-0.40</td>
<td>0.31-0.43</td>
<td>0.3</td>
<td>&lt;0.005</td>
<td>0.06</td>
<td>0.37-0.44</td>
<td>0.22</td>
<td>0.27</td>
<td>1.21</td>
<td>0.3</td>
<td>0.3</td>
<td>0.31</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>&lt;0.035</td>
<td>0.01-</td>
<td>0.01</td>
<td>0.001</td>
<td>0.005</td>
<td>0.0042</td>
<td>0.003</td>
<td>0.01</td>
<td>0.001</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>&lt;0.030</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
<td>0.004</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>0.004</td>
<td>0.003</td>
<td>0.001</td>
<td>0.002</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.01-0.03</td>
<td>0.19-</td>
<td>0.036</td>
<td>0.055</td>
<td>0.055</td>
<td>0.1</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
<td>0.002</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.002</td>
<td>0.004</td>
<td>&lt;0.01</td>
<td>0.008</td>
<td>&lt;0.005</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
<td>0.002</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>&lt;0.01</td>
<td>0.08</td>
<td>0.07-0.09</td>
<td>0.07</td>
<td>0.0022</td>
<td>0.01</td>
<td>0.14</td>
<td>0.48</td>
<td>0.048</td>
<td>0.34</td>
<td>0.05</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>3 x 10^-7</td>
<td>0.02</td>
<td>0.0036</td>
<td>0.03</td>
<td>0.03</td>
<td>0.01</td>
<td>0.14</td>
<td>0.48</td>
<td>0.048</td>
<td>0.34</td>
<td>0.05</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.01</td>
<td>0.14-</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.25</td>
<td>0.20</td>
<td>0.20</td>
<td>0.18</td>
<td>0.33</td>
<td>0.3</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;0.01</td>
<td>0.004-0.01</td>
<td>0.033</td>
<td>0.003</td>
<td>0.2</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.29</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.009</td>
<td>0.010</td>
<td>0.047</td>
<td>0.04</td>
<td>0.011</td>
<td>0.014</td>
<td>0.071</td>
<td>0.071</td>
<td>0.071</td>
<td>0.013</td>
<td>0.024</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>4 x 10^-7</td>
<td>&lt;0.0005</td>
<td>0.001</td>
<td>0.034</td>
<td>0.27</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Table 6.3.2. Composition of austenitic steels

<table>
<thead>
<tr>
<th></th>
<th>D9</th>
<th>14Cr-16Ni-2Mo</th>
<th>1.4970</th>
<th>316L</th>
<th>1.4984</th>
<th>304L</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.04</td>
<td>0.058</td>
<td>0.46</td>
<td>0.012-0.02</td>
<td>0.06</td>
<td>0.020</td>
</tr>
<tr>
<td>Cr</td>
<td>13.6</td>
<td>14.14</td>
<td>16.5</td>
<td>16-18</td>
<td>17-19</td>
<td>18.50</td>
</tr>
<tr>
<td>Ni</td>
<td>13.6</td>
<td>15.85</td>
<td>13.8</td>
<td>10-17.392</td>
<td>10-12</td>
<td>8.31</td>
</tr>
<tr>
<td>Mo</td>
<td>1.67</td>
<td>2.29</td>
<td>0.66</td>
<td>2-2.75</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>2.1</td>
<td>1.54</td>
<td>1.91</td>
<td>0.2-2</td>
<td>0-2</td>
<td>1.67</td>
</tr>
<tr>
<td>Si</td>
<td>0.85</td>
<td>0.50</td>
<td>0.89</td>
<td>0.1-1</td>
<td>0.75</td>
<td>0.49</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td>0.012</td>
<td>0.024-0.19</td>
<td>0.026</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>0.009</td>
<td>0.0005-0.03</td>
<td>0.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td></td>
<td>0.06-0.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.003</td>
<td></td>
<td>0.02-0.1</td>
<td>0.069</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.30</td>
<td>0.22</td>
<td>0.43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>0.010</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.012</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6.3.3. Fe-Cr steels in stagnant LBE

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Time (hours)</th>
<th>[O] (%wt.)</th>
<th>OCS</th>
<th>Surface sample/LBE volume ratio (cm³/LBE)</th>
<th>Oxide thickness/dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>F82H</td>
<td>476</td>
<td>700</td>
<td>Saturation</td>
<td>Argon</td>
<td>18</td>
<td>34</td>
<td>Oxidation</td>
<td></td>
<td>[Fazio, 2001]</td>
</tr>
<tr>
<td>F82H</td>
<td>476</td>
<td>1200</td>
<td>Saturation</td>
<td>Argon</td>
<td>18</td>
<td>34</td>
<td>Oxidation</td>
<td></td>
<td>[Fazio, 2001]</td>
</tr>
<tr>
<td>F82H*</td>
<td>400</td>
<td>100</td>
<td>Argon</td>
<td>9.7/0.035</td>
<td>Weight gain: -3 mdd¹</td>
<td>Weight loss: 36 mdd</td>
<td>[Soler, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H*</td>
<td>600</td>
<td>100</td>
<td>Argon</td>
<td>9.7/0.035</td>
<td>Weight loss: 52 mdd</td>
<td>Weight loss: 4 mdd</td>
<td>[Soler, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H-preox.*</td>
<td>600</td>
<td>665</td>
<td>Argon</td>
<td>9.7/0.035</td>
<td>Weight loss: 14 mdd</td>
<td>Weight loss: 2.5 mdd</td>
<td>[Soler, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H-preox.*</td>
<td>600</td>
<td>100</td>
<td>Argon</td>
<td>9.7/0.035</td>
<td>Weight loss: 11 mdd</td>
<td>Weight loss: 2 mdd</td>
<td>[Soler, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H-preox.*</td>
<td>600</td>
<td>100</td>
<td>Argon</td>
<td>9.7/0.035</td>
<td>Weight loss: 17 mdd</td>
<td>Weight loss: 2 mdd</td>
<td>[Soler, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H*</td>
<td>400</td>
<td>100</td>
<td>Argon + 10%H2</td>
<td>9.7/0.035</td>
<td>Weight gain: -1 mdd</td>
<td>Weight loss: 3 mdd</td>
<td>[Soler, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H*</td>
<td>600</td>
<td>100</td>
<td>Argon + 10%H2</td>
<td>9.7/0.035</td>
<td>Weight loss: 11 mdd</td>
<td>Weight loss: 2 mdd</td>
<td>[Soler, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H-preox.*</td>
<td>600</td>
<td>100</td>
<td>Argon + 10%H2</td>
<td>9.7/0.035</td>
<td>Weight loss: 17 mdd</td>
<td>Weight loss: 2 mdd</td>
<td>[Soler, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H-preox.*</td>
<td>600</td>
<td>665</td>
<td>Argon + 10%H2</td>
<td>9.7/0.035</td>
<td>Weight loss: 2 mdd</td>
<td>Weight loss: 2 mdd</td>
<td>[Soler, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>550</td>
<td>500</td>
<td>Saturation</td>
<td>Ar</td>
<td>10.8/14</td>
<td>20</td>
<td>Oxidation</td>
<td></td>
<td>[Kurata, 2002]</td>
</tr>
<tr>
<td>F82H</td>
<td>535</td>
<td>1000</td>
<td>3 x 10⁻⁷</td>
<td>Ar-H2H2O</td>
<td>5/0.004</td>
<td>20</td>
<td>Oxidation</td>
<td></td>
<td>[Gómez, 2002]</td>
</tr>
<tr>
<td>F82H</td>
<td>550</td>
<td>1000</td>
<td>4 x 10⁻⁷</td>
<td>Ar-H2H2O</td>
<td>5/0.004</td>
<td>15</td>
<td>Oxidation</td>
<td>Coexistence with oxide</td>
<td>[Gómez, 2002]</td>
</tr>
<tr>
<td>F82H</td>
<td>535</td>
<td>500</td>
<td>3 x 10⁻⁷</td>
<td>Ar-H2H2O</td>
<td>5/0.004</td>
<td>15</td>
<td>Oxidation</td>
<td></td>
<td>[Gómez, 2002]</td>
</tr>
<tr>
<td>F82H</td>
<td>550</td>
<td>100</td>
<td>4 x 10⁻⁷</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>-18</td>
<td>Dissolution</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>100</td>
<td>8 x 10⁻⁷</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>-5</td>
<td>Dissolution</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>F82H</td>
<td>535</td>
<td>3000</td>
<td>3 x 10⁻⁷</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>-13</td>
<td>Dissolution</td>
<td>Rests of oxide layer</td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>F82H</td>
<td>550</td>
<td>3000</td>
<td>4 x 10⁻⁷</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>-17</td>
<td>Dissolution</td>
<td>No rests of oxide layer</td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>F82H</td>
<td>535</td>
<td>500</td>
<td>3 x 10⁻⁶</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>-8</td>
<td>Dissolution</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>F82H</td>
<td>550</td>
<td>500</td>
<td>4 x 10⁻⁶</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>-14</td>
<td>Dissolution</td>
<td>Rests of oxide layer (Cr enrichment)</td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>500</td>
<td>8 x 10⁻⁶</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>-21</td>
<td>Dissolution</td>
<td>Rests of oxide layer</td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>F82H</td>
<td>535</td>
<td>3000</td>
<td>3 x 10⁻⁶</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>-10</td>
<td>Dissolution</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>F82H</td>
<td>550</td>
<td>3000</td>
<td>4 x 10⁻⁶</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>-5</td>
<td>Dissolution</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>3000</td>
<td>8 x 10⁻⁵</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>-80</td>
<td>Dissolution</td>
<td>Coexistence with oxide layer</td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>F82H</td>
<td>450</td>
<td>3000</td>
<td>6 x 10⁻⁸</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>11</td>
<td>Oxidation</td>
<td>Coexistence with oxide layer</td>
<td>[Gómez, 2004]</td>
</tr>
<tr>
<td>F82H-preox</td>
<td>450</td>
<td>3000</td>
<td>6 x 10⁻⁸</td>
<td>H2H2O</td>
<td>5/0.004</td>
<td>14</td>
<td>Oxidation</td>
<td>Oxide layer broken in some zones</td>
<td>[Gómez, 2004]</td>
</tr>
</tbody>
</table>
Table 6.3.3. Fe-Cr steels in stagnant LBE (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Time (hours)</th>
<th>[O] (%wt.)</th>
<th>OCS</th>
<th>Surface sample/LBE volume ratio (cm²/l)</th>
<th>Oxide thickness/dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>F82H</td>
<td>600</td>
<td>100</td>
<td>4.7 × 10⁻⁸</td>
<td>Ar + H₂ + H₂O</td>
<td>9.7/0.035</td>
<td>17</td>
<td>Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>500</td>
<td>4.7 × 10</td>
<td>Ar + H₂ + H₂O</td>
<td>9.7/0.035</td>
<td>48</td>
<td>Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>1500</td>
<td>4.7 × 10</td>
<td>Ar + H₂ + H₂O</td>
<td>9.7/0.035</td>
<td>90</td>
<td>Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>100</td>
<td>2 × 10⁻³</td>
<td>Ar (saturation)</td>
<td>9.7/0.035</td>
<td>13</td>
<td>Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>500</td>
<td>2 × 10⁻³</td>
<td>Ar (saturation)</td>
<td>9.7/0.035</td>
<td>35</td>
<td>Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>1500</td>
<td>2 × 10⁻³</td>
<td>Ar (saturation)</td>
<td>9.7/0.035</td>
<td>24</td>
<td>Oxidation</td>
<td>Pb-Bi penetration</td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>450</td>
<td>100</td>
<td>6 × 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td></td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>450</td>
<td>500</td>
<td>3 × 10⁻⁴</td>
<td>Ar (saturation)</td>
<td>9.7/0.035</td>
<td>4</td>
<td>Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>450</td>
<td>1500</td>
<td>6 × 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td></td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>500</td>
<td>1.1 × 10⁻⁸</td>
<td>Ar + H₂</td>
<td>9.7/0.035</td>
<td></td>
<td>Oxidation</td>
<td>Coexistence of dissolution and oxidation</td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>100</td>
<td>1.1 × 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>15</td>
<td>Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>1500</td>
<td>1.1 × 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>-40</td>
<td>Dissolution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>450</td>
<td>500, 2400</td>
<td>1.1 × 10⁻⁸</td>
<td>Ar + H₂</td>
<td>9.7/0.035</td>
<td></td>
<td>Oxidation</td>
<td>Cr oxidation</td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>600</td>
<td>1500</td>
<td>1.1 × 10⁻⁸</td>
<td>Ar + H₂</td>
<td>9.7/0.035</td>
<td></td>
<td>Dissolution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>450</td>
<td>3000</td>
<td>3.2 × 10⁻⁴</td>
<td>Ar-saturation</td>
<td>21.6/0.7</td>
<td>8.39</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F82H</td>
<td>550</td>
<td>3000</td>
<td>1.2 × 10⁻³</td>
<td>Ar-saturation</td>
<td>21.6/0.7</td>
<td>13.95</td>
<td>Oxidation</td>
<td>Internal oxidation (6.19 μm)</td>
<td></td>
</tr>
<tr>
<td>Mod9Cr-1Mo</td>
<td>450</td>
<td>3000</td>
<td>3.2 × 10⁻⁴</td>
<td>Ar-saturation</td>
<td>21.6/0.7</td>
<td>8.41</td>
<td>Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mod9Cr-1Mo</td>
<td>550</td>
<td>3000</td>
<td>1.2 × 10⁻³</td>
<td>Ar-saturation</td>
<td>21.6/0.7</td>
<td>13.97</td>
<td>Oxidation</td>
<td>Internal oxidation (7.32 μm)</td>
<td></td>
</tr>
<tr>
<td>9Cr-1Mo</td>
<td>550</td>
<td>500</td>
<td>Saturation</td>
<td>Ar</td>
<td>10.8/</td>
<td>20</td>
<td>Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>550</td>
<td>100</td>
<td>4 × 10⁻⁷</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>-16</td>
<td>Dissolution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>600</td>
<td>100</td>
<td>8 × 10⁻⁷</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>-5</td>
<td>Dissolution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>535</td>
<td>3000</td>
<td>3 × 10⁻⁷</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>-26</td>
<td>Dissolution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>550</td>
<td>3000</td>
<td>4 × 10⁻⁷</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>-34</td>
<td>Dissolution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>535</td>
<td>500</td>
<td>3 × 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>18</td>
<td>Oxidation</td>
<td>Broken and detached</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>550</td>
<td>500</td>
<td>4 × 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>17</td>
<td>Oxidation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>600</td>
<td>500</td>
<td>8 × 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>-21</td>
<td>Dissolution</td>
<td>Rest of oxide layer (Cr enrichment)</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>535</td>
<td>3000</td>
<td>3 × 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>No oxidation/no dissolution</td>
<td></td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>Material</td>
<td>T (°C)</td>
<td>Time (hours)</td>
<td>[O] (%wt.)</td>
<td>OCS</td>
<td>Surface sample/LBE volume ratio (cm²/l)</td>
<td>Oxide thickness/dissolution depth (microns)</td>
<td>Remark 1</td>
<td>Remark 2</td>
<td>Ref.</td>
</tr>
<tr>
<td>-----------</td>
<td>--------</td>
<td>--------------</td>
<td>------------</td>
<td>--------------</td>
<td>---------------------------------------</td>
<td>---------------------------------------------</td>
<td>---------------------------------------</td>
<td>--------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>T91</td>
<td>550</td>
<td>3000</td>
<td>4 × 10⁻²</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>-20</td>
<td>Dissolution</td>
<td>[Martin, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>600</td>
<td>3000</td>
<td>8 × 10⁻³</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>-130</td>
<td>Dissolution Coexistence with oxide layer</td>
<td>[Martin, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>450</td>
<td>3000</td>
<td>6 × 10⁻³</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>30</td>
<td>Oxidation Broken oxide layer</td>
<td>[Gómez, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91 preox</td>
<td>450</td>
<td>3000</td>
<td>6 × 10⁻³</td>
<td>H₂/H₂O</td>
<td>5.0/0.004</td>
<td>12</td>
<td>Oxidation Broken in some zones</td>
<td>[Gómez, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>600</td>
<td>100</td>
<td>4.7 × 10⁻⁴</td>
<td>Ar + H₂ + H₂O</td>
<td>9.7/0.035</td>
<td>20</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>600</td>
<td>500</td>
<td>4.7 × 10⁻⁴</td>
<td>Ar + H₂ + H₂O</td>
<td>9.7/0.035</td>
<td>41</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>600</td>
<td>1500</td>
<td>2 × 10⁻³</td>
<td>Ar (saturation)</td>
<td>9.7/0.035</td>
<td>41</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>600</td>
<td>100</td>
<td>2 × 10⁻⁴</td>
<td>Ar (saturation)</td>
<td>9.7/0.035</td>
<td>40</td>
<td>Oxidation Pb-Bi penetration</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>450</td>
<td>500</td>
<td>3 × 10⁻⁴</td>
<td>Ar (saturation)</td>
<td>9.7/0.035</td>
<td>32</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>450</td>
<td>100</td>
<td>6 × 10⁻⁴</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>20</td>
<td>Oxidation Cr oxide, discontinuous oxide</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>450</td>
<td>1500</td>
<td>6 × 10⁻⁴</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>10</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>600</td>
<td>100</td>
<td>1.1 × 10⁻⁴</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>22</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>600</td>
<td>1500</td>
<td>1.1 × 10⁻⁴</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>-10</td>
<td>Dissolution</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>450</td>
<td>500, 2400</td>
<td>1.1 × 10⁻⁴</td>
<td>Ar + H₂</td>
<td>9.7/0.035</td>
<td>5</td>
<td>Oxidation Cr oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>600</td>
<td>500</td>
<td>1.1 × 10⁻⁴</td>
<td>Ar + H₂</td>
<td>9.7/0.035</td>
<td>15</td>
<td>Oxidation Thin oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>600</td>
<td>1500</td>
<td>1.1 × 10⁻⁴</td>
<td>Ar + H₂</td>
<td>9.7/0.035</td>
<td>-13</td>
<td>Dissolution</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>450</td>
<td>550</td>
<td>3.14 × 10⁻⁴</td>
<td>Ar N60</td>
<td>4/</td>
<td>10</td>
<td>Oxidation</td>
<td>[Gnecco, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>550</td>
<td>550</td>
<td>1.17 × 10⁻⁴</td>
<td>Ar N60</td>
<td>4/</td>
<td>7</td>
<td>Oxidation</td>
<td>[Gnecco, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91*</td>
<td>600</td>
<td>550</td>
<td>1.17 × 10⁻⁴</td>
<td>Ar N60</td>
<td>4/</td>
<td>14</td>
<td>Oxidation</td>
<td>[Gnecco, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91*</td>
<td>350</td>
<td>1000</td>
<td>4/</td>
<td>Ar N60</td>
<td>2/</td>
<td>2</td>
<td>Oxidation</td>
<td>[Gnecco, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91*</td>
<td>450</td>
<td>1000</td>
<td>4/</td>
<td>Ar N60</td>
<td>12/</td>
<td>10</td>
<td>Oxidation</td>
<td>[Gnecco, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>550</td>
<td>1000</td>
<td>1.17 × 10⁻³</td>
<td>Ar N60</td>
<td>4/</td>
<td>10</td>
<td>Oxidation</td>
<td>[Gnecco, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91*</td>
<td>600</td>
<td>1000</td>
<td>4/</td>
<td>Ar N60</td>
<td>3-4</td>
<td>7</td>
<td>Oxidation</td>
<td>[Gnecco, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>550</td>
<td>550</td>
<td>3.9 × 10⁻⁷</td>
<td>Ar + 5%H₂</td>
<td>4/</td>
<td>-7</td>
<td>Dissolution</td>
<td>[Gnecco, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>450</td>
<td>2000</td>
<td>3.9 × 10⁻⁷</td>
<td>Ar + 5%H₂</td>
<td>4/</td>
<td>-3</td>
<td>Dissolution</td>
<td>[Gnecco, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>550</td>
<td>2000</td>
<td>3.9 × 10⁻⁷</td>
<td>Ar + 5%H₂</td>
<td>4/</td>
<td>-30</td>
<td>Dissolution</td>
<td>[Gnecco, 2004]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>470</td>
<td>7800</td>
<td>Saturation</td>
<td>Ar-H₂/H₂O</td>
<td>4/</td>
<td>30</td>
<td>Oxidation</td>
<td>[Martinelli, 2005]</td>
<td></td>
</tr>
<tr>
<td>12Cr,ODS-M</td>
<td>500</td>
<td>800</td>
<td>1 × 10⁻⁶</td>
<td>Ar-H₂/H₂O</td>
<td>4/</td>
<td>10</td>
<td>Oxidation</td>
<td>[Furukawa, 2004]</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>T (°C)</td>
<td>Time (hours)</td>
<td>[O] (%w.t.)</td>
<td>OCS</td>
<td>Surface sample/LBE volume ratio (cm²/l)</td>
<td>Oxide thickness/dissolution depth (microns)</td>
<td>Remark 1</td>
<td>Remark 2</td>
<td>Ref.</td>
</tr>
<tr>
<td>---------------</td>
<td>--------</td>
<td>--------------</td>
<td>-------------</td>
<td>--------------</td>
<td>-----------------------------------------</td>
<td>--------------------------------------------</td>
<td>---------------------------------------------</td>
<td>---------------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>12Cr,ODS-M</td>
<td>500</td>
<td>2000</td>
<td>$1 \times 10^{-6}$</td>
<td>Ar-H₂/H₂O</td>
<td>Oxidation</td>
<td>Diffusion+Fe-Cr-O+Fe-O+porous Fe-O</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12Cr,ODS-M</td>
<td>500</td>
<td>5000</td>
<td>$1 \times 10^{-6}$</td>
<td>Ar-H₂/H₂O</td>
<td>Dissolution</td>
<td>Dissolution at some points</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12Cr</td>
<td>550</td>
<td>800</td>
<td>$1 \times 10^{-6}$</td>
<td>Ar-H₂/H₂O</td>
<td>15</td>
<td>Oxidation</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12Cr</td>
<td>550</td>
<td>2000</td>
<td>$1 \times 10^{-6}$</td>
<td>Ar-H₂/H₂O</td>
<td>25</td>
<td>Oxidation</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODS-M</td>
<td>550</td>
<td>800</td>
<td>$1 \times 10^{-6}$</td>
<td>Ar-H₂/H₂O</td>
<td>20</td>
<td>Dissolution</td>
<td>Dissolution at some points</td>
<td>[Furukawa, 2004]</td>
<td></td>
</tr>
<tr>
<td>ODS-M</td>
<td>550</td>
<td>2000</td>
<td>$1 \times 10^{-6}$</td>
<td>Ar-H₂/H₂O</td>
<td>30</td>
<td>Oxidation</td>
<td>Diffusion+Fe-Cr-O+Fe-O+porous Fe-O</td>
<td>[Furukawa, 2004]</td>
<td></td>
</tr>
<tr>
<td>Eurofer 97</td>
<td>550</td>
<td>550</td>
<td>$1.17 \times 10^{-3}$</td>
<td>Ar N60</td>
<td>4/</td>
<td>6</td>
<td>Oxidation</td>
<td>Dissolution at some points</td>
<td>[Gnecco, 2004]</td>
</tr>
<tr>
<td>EM10</td>
<td>550</td>
<td>100</td>
<td>$4 \times 10^{-7}$</td>
<td>H₂O/H₂O</td>
<td>5/0.004</td>
<td>-14</td>
<td>Dissolution</td>
<td>[Martin, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>535</td>
<td>3000</td>
<td>$3 \times 10^{-3}$</td>
<td>H₂O/H₂O</td>
<td>5/0.004</td>
<td>-45</td>
<td>Dissolution</td>
<td>[Martin, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>535</td>
<td>3000</td>
<td>$4 \times 10^{-7}$</td>
<td>H₂O/H₂O</td>
<td>5/0.004</td>
<td>-65</td>
<td>Dissolution</td>
<td>[Martin, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>535</td>
<td>3000</td>
<td>$3 \times 10^{-6}$</td>
<td>H₂O/H₂O</td>
<td>5/0.004</td>
<td>14</td>
<td>Oxidation</td>
<td>[Martin, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>550</td>
<td>500</td>
<td>$4 \times 10^{-6}$</td>
<td>H₂O/H₂O</td>
<td>5/0.004</td>
<td>10</td>
<td>Oxidation</td>
<td>[Martin, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>600</td>
<td>500</td>
<td>$8 \times 10^{-6}$</td>
<td>H₂O/H₂O</td>
<td>5/0.004</td>
<td>-21</td>
<td>Dissolution</td>
<td>Rest of oxide layer (Cr enrichment)</td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>EM10</td>
<td>535</td>
<td>3000</td>
<td>$3 \times 10^{-6}$</td>
<td>H₂O/H₂O</td>
<td>5/0.004</td>
<td>-10</td>
<td>Dissolution</td>
<td>[Martin, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>550</td>
<td>3000</td>
<td>$4 \times 10^{-6}$</td>
<td>H₂O/H₂O</td>
<td>5/0.004</td>
<td>-15</td>
<td>Dissolution</td>
<td>[Martin, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>600</td>
<td>3000</td>
<td>$8 \times 10^{-3}$</td>
<td>H₂O/H₂O</td>
<td>5/0.004</td>
<td>-16</td>
<td>Dissolution</td>
<td>Coexistence with oxide layer</td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>EM10</td>
<td>450</td>
<td>3000</td>
<td>$6 \times 10^{-4}$</td>
<td>H₂O/H₂O</td>
<td>5/0.004</td>
<td>11</td>
<td>Oxidation</td>
<td>Oxide layer detached in zones</td>
<td>[Gómez, 2004]</td>
</tr>
<tr>
<td>EM10-preox</td>
<td>450</td>
<td>3000</td>
<td>$6 \times 10^{-4}$</td>
<td>H₂O/H₂O</td>
<td>5/0.004</td>
<td>9</td>
<td>Oxidation</td>
<td>Broken in some zones</td>
<td>[Gómez, 2004]</td>
</tr>
<tr>
<td>EM10</td>
<td>600</td>
<td>100</td>
<td>$4.7 \times 10^{-10}$</td>
<td>Ar + H₂ + H₂O</td>
<td>9.7/0.035</td>
<td>22</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>600</td>
<td>500</td>
<td>$4.7 \times 10^{-10}$</td>
<td>Ar + H₂ + H₂O</td>
<td>9.7/0.035</td>
<td>41</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>600</td>
<td>1500</td>
<td>$4.7 \times 10^{-10}$</td>
<td>Ar + H₂ + H₂O</td>
<td>9.7/0.035</td>
<td>95</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>T (°C)</td>
<td>Time (hours)</td>
<td>[O] (%wt.)</td>
<td>OCS</td>
<td>Surface sample/LBE volume ratio (cm²/l)</td>
<td>Oxide thickness/dissolution depth (microns)</td>
<td>Remark 1</td>
<td>Remark 2</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------</td>
<td>--------</td>
<td>--------------</td>
<td>------------</td>
<td>-----</td>
<td>----------------------------------------</td>
<td>---------------------------------------------</td>
<td>----------</td>
<td>---------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>EM10</td>
<td>600</td>
<td>100</td>
<td>$2 \times 10^{-3}$</td>
<td>Ar (saturation)</td>
<td>9.7/0.035</td>
<td>9</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>600</td>
<td>500</td>
<td>$2 \times 10^{-3}$</td>
<td>Ar (saturation)</td>
<td>9.7/0.035</td>
<td>37</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>600</td>
<td>1500</td>
<td>$2 \times 10^{-3}$</td>
<td>Ar (saturation)</td>
<td>9.7/0.035</td>
<td>43</td>
<td>Oxidation Pb-Bi penetration</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>450</td>
<td>500</td>
<td>$3 \times 10^{-4}$</td>
<td>Ar (saturation)</td>
<td>9.7/0.035</td>
<td>4</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>450</td>
<td>100</td>
<td>$6 \times 10^{-3}$</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>7</td>
<td>Oxidation Cr oxide</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>450</td>
<td>1500</td>
<td>$6 \times 10^{-3}$</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>15</td>
<td>Oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>600</td>
<td>100</td>
<td>$1.1 \times 10^{-3}$</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>-10</td>
<td>Dissolution</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>600</td>
<td>1500</td>
<td>$1.1 \times 10^{-3}$</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>2</td>
<td>Oxidation Thin oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>600</td>
<td>500</td>
<td>$1.1 \times 10^{-3}$</td>
<td>Ar+H₂</td>
<td>9.7/0.035</td>
<td>7</td>
<td>Oxidation Slight</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>300</td>
<td>1500</td>
<td>Saturation</td>
<td>Argon</td>
<td>n.m.</td>
<td>Oxidation</td>
<td>[Fazio, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>300</td>
<td>5000</td>
<td>Saturation</td>
<td>Argon</td>
<td>&lt;1</td>
<td>Oxidation</td>
<td>[Fazio, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>400</td>
<td>1500</td>
<td>Saturation</td>
<td>Argon</td>
<td>1</td>
<td>Oxidation</td>
<td>[Fazio, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>400</td>
<td>5000</td>
<td>Saturation</td>
<td>Argon</td>
<td>5</td>
<td>Oxidation</td>
<td>[Fazio, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>476</td>
<td>700</td>
<td>Saturation</td>
<td>Argon</td>
<td>11</td>
<td>Oxidation</td>
<td>[Fazio, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>476</td>
<td>1200</td>
<td>Saturation</td>
<td>Argon</td>
<td>16</td>
<td>Oxidation</td>
<td>[Fazio, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>300</td>
<td>1500, 3000, 5000</td>
<td>$1.84 \times 10^{-5}$</td>
<td>Argon</td>
<td>Oxidation Thin</td>
<td>[Benamati, 2002]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>400</td>
<td>1500, 3000</td>
<td>$1.41 \times 10^{-4}$</td>
<td>Argon</td>
<td>Oxidation Thin</td>
<td>[Benamati, 2002]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>400</td>
<td>5000</td>
<td>$1.41 \times 10^{-4}$</td>
<td>Argon</td>
<td>Oxidation Thicker</td>
<td>[Benamati, 2002]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>550</td>
<td>1500</td>
<td>$1.17 \times 10^{-1}$</td>
<td>Argon</td>
<td>Dissolution</td>
<td>[Benamati, 2002]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>550</td>
<td>3000, 5000</td>
<td>$1.17 \times 10^{-1}$</td>
<td>Argon</td>
<td>Dissolution Severe Coexistence with thin oxide</td>
<td>[Benamati, 2002]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet</td>
<td>300</td>
<td>1500, 3000</td>
<td>$1.85 \times 10^{-3}$</td>
<td>Saturation</td>
<td>Oxidation Thin</td>
<td>[Bin, 2003]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet</td>
<td>400</td>
<td>1500, 3000</td>
<td>$1.41 \times 10^{-4}$</td>
<td>Saturation</td>
<td>Oxidation Thin</td>
<td>[Bin, 2003]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet</td>
<td>550</td>
<td>1500</td>
<td>$1.17 \times 10^{-1}$</td>
<td>Saturation</td>
<td>Dissolution Coexistence with oxide layer</td>
<td>[Bin, 2003]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6.3.3. Fe-Cr steels in stagnant LBE (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Time (hours)</th>
<th>[O] (%wt.)</th>
<th>OCS</th>
<th>Surface sample/LBE volume ratio (cm²/l)</th>
<th>Oxide thickness/dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manet</td>
<td>550</td>
<td>3000, 5000</td>
<td>1.17 × 10⁻³</td>
<td>Saturation</td>
<td>Dissolution</td>
<td></td>
<td></td>
<td></td>
<td>[Bin, 2003]</td>
</tr>
<tr>
<td>Manet</td>
<td>300</td>
<td>5000</td>
<td>1.85 × 10⁻³</td>
<td>Saturation</td>
<td>Oxidation</td>
<td></td>
<td></td>
<td></td>
<td>[Bin, 2003]</td>
</tr>
<tr>
<td>Manet</td>
<td>400</td>
<td>5000</td>
<td>1.41 × 10⁻³</td>
<td>Saturation</td>
<td>Oxidation Double layer</td>
<td></td>
<td></td>
<td></td>
<td>[Bin, 2003]</td>
</tr>
<tr>
<td>56T5</td>
<td>&gt;480</td>
<td>3000</td>
<td>5 × 10⁻⁷</td>
<td>3.42/</td>
<td>Dissolution Intergranular attack</td>
<td>[Deloffre, 2002]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>56T5</td>
<td>400-480</td>
<td>3000</td>
<td>5 × 10⁻⁷</td>
<td>3.42/</td>
<td>Fe deposits</td>
<td>[Deloffre, 2002]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>56T5</td>
<td>&lt;400</td>
<td>3000</td>
<td>5 × 10⁻⁷</td>
<td>3.42/</td>
<td>Oxidation</td>
<td>[Deloffre, 2002]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODS</td>
<td>500</td>
<td>10000</td>
<td>10⁻⁵</td>
<td>H₂/H₂O</td>
<td>Oxidation</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODS</td>
<td>550</td>
<td>5000</td>
<td>10⁻⁵</td>
<td>H₂/H₂O</td>
<td>Oxidation</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODS</td>
<td>600</td>
<td>2000</td>
<td>10⁻⁵</td>
<td>H₂/H₂O</td>
<td>Oxidation Spinel + dissolution zones</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODS</td>
<td>650</td>
<td>5000</td>
<td>10⁻⁵</td>
<td>H₂/H₂O</td>
<td>Oxidation Spinel + dissolution zones</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODS</td>
<td>650</td>
<td>10000</td>
<td>10⁻⁵</td>
<td>H₂/H₂O</td>
<td>Dissolution partial</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODS</td>
<td>650</td>
<td>5000</td>
<td>10⁻⁵</td>
<td>H₂/H₂O</td>
<td>Dissolution</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODS</td>
<td>650</td>
<td>2000</td>
<td>10⁻⁵</td>
<td>H₂/H₂O</td>
<td>Oxidation Rehealing</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODS</td>
<td>650</td>
<td>5000</td>
<td>10⁻⁵</td>
<td>H₂/H₂O</td>
<td>Oxidation LBE inclusion pores</td>
<td>[Furukawa, 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT9</td>
<td>500</td>
<td>800</td>
<td>1 × 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>8</td>
<td>Oxidation COSTA</td>
<td>[Müller, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT9</td>
<td>500</td>
<td>2000</td>
<td>1 × 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>8</td>
<td>Oxidation COSTA</td>
<td>[Müller, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT9</td>
<td>500</td>
<td>5000</td>
<td>1 × 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>60-70</td>
<td>Oxidation Porosity layer at the interface</td>
<td>[Müller, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT9</td>
<td>550</td>
<td>800, 2000</td>
<td>1 × 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>50</td>
<td>Oxidation</td>
<td>[Müller, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT9</td>
<td>550</td>
<td>5000</td>
<td>1 × 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>50</td>
<td>Oxidation</td>
<td>[Müller, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT9</td>
<td>600</td>
<td>800, 2000</td>
<td>1 × 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>50</td>
<td>Oxidation Pb-Bi pentration</td>
<td>[Müller, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>410ss</td>
<td>450</td>
<td>3000</td>
<td>3.2 × 10⁻⁴</td>
<td>Ar-saturation 21.6/0.7 2.83</td>
<td>Oxidation</td>
<td>[Kurat, 2005]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>410ss</td>
<td>350</td>
<td>3000</td>
<td>1.2 × 10⁻⁴</td>
<td>Ar-saturation 21.6/0.7 5.42</td>
<td>Oxidation</td>
<td>[Kurat, 2005]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>410ss, 430ss</td>
<td>550</td>
<td>500</td>
<td>Saturation</td>
<td>Ar</td>
<td>10.8/</td>
<td>Oxidation Thin oxide layer</td>
<td>[Kurat, 2002]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Not clarified enough (oxygen content information missed).
1. Milligrams/decimetre-day. 1 decimeter = 100 cm².
### Table 6.3.4. Fe-Cr-Ni steels in stagnant LBE

<table>
<thead>
<tr>
<th>Material</th>
<th>T (ºC)</th>
<th>Time (hours)</th>
<th>[O] (%wt.)</th>
<th>OCS</th>
<th>Surface sample/LBE volume ratio (cm²/l)</th>
<th>Oxide thickness/dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>14Cr-16Ni-2Mo</td>
<td>550</td>
<td>500</td>
<td>Saturation</td>
<td>Argon</td>
<td>10.8/</td>
<td>Oxidation</td>
<td>Thin</td>
<td></td>
<td>[Kurata, 2002]</td>
</tr>
<tr>
<td>316L</td>
<td>300, 400</td>
<td>1500</td>
<td>Saturation</td>
<td>Argon</td>
<td>n.m.</td>
<td>Oxidation</td>
<td></td>
<td></td>
<td>[Fazio, 2001]</td>
</tr>
<tr>
<td>316L</td>
<td>300</td>
<td>5000</td>
<td>Saturation</td>
<td>Argon</td>
<td>&lt;1</td>
<td>Oxidation</td>
<td></td>
<td></td>
<td>[Fazio, 2001]</td>
</tr>
<tr>
<td>316L</td>
<td>400</td>
<td>5000</td>
<td>Saturation</td>
<td>Argon</td>
<td>1</td>
<td>Oxidation</td>
<td></td>
<td></td>
<td>[Fazio, 2001]</td>
</tr>
<tr>
<td>316L</td>
<td>476</td>
<td>700</td>
<td>Saturation</td>
<td>Argon</td>
<td>n.m.</td>
<td>Oxidation</td>
<td></td>
<td></td>
<td>[Fazio, 2001]</td>
</tr>
<tr>
<td>316L</td>
<td>476</td>
<td>1200</td>
<td>Saturation</td>
<td>Argon</td>
<td>2-4</td>
<td>Oxidation</td>
<td></td>
<td></td>
<td>[Fazio, 2001]</td>
</tr>
<tr>
<td>316L</td>
<td>300</td>
<td>1500, 3000, 5000</td>
<td>1.84 × 10⁻⁵</td>
<td>Argon</td>
<td>Oxidation</td>
<td>Thin</td>
<td></td>
<td></td>
<td>[Benamati, 2002]</td>
</tr>
<tr>
<td>316L</td>
<td>400</td>
<td>1500, 3000, 5000</td>
<td>1.41 × 10⁻⁴</td>
<td>Argon</td>
<td>Oxidation</td>
<td>Thin</td>
<td></td>
<td></td>
<td>[Benamati, 2002]</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>1500</td>
<td>1.17 × 10⁻³</td>
<td>Argon</td>
<td>Oxidation</td>
<td>Thin-spongy</td>
<td></td>
<td></td>
<td>[Benamati, 2002]</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>3000, 5000</td>
<td>1.17 × 10⁻³</td>
<td>Argon</td>
<td>Dissolution</td>
<td>Pb-Bi penetration</td>
<td></td>
<td></td>
<td>[Benamati, 2002]</td>
</tr>
<tr>
<td>316L-Preox.</td>
<td>&gt;450</td>
<td>3000</td>
<td>5 × 10⁻⁷</td>
<td>3.42/</td>
<td>10-35</td>
<td>Oxidation</td>
<td>Porous layer</td>
<td></td>
<td>[Deloffre, 2002]</td>
</tr>
<tr>
<td>316L</td>
<td>360-450</td>
<td>3000</td>
<td>5 × 10⁻⁷</td>
<td>3.42/</td>
<td>Oxidation</td>
<td>Crystals. Fe rich at high T, Cr rich at low T.</td>
<td></td>
<td></td>
<td>[Deloffre, 2002]</td>
</tr>
<tr>
<td>316L</td>
<td>&lt;360</td>
<td>3000</td>
<td>5 × 10⁻⁷</td>
<td>3.42/</td>
<td>Oxidation</td>
<td>No deposits</td>
<td></td>
<td></td>
<td>[Deloffre, 2002]</td>
</tr>
<tr>
<td>316FBR</td>
<td>500</td>
<td>800, 200, 5000</td>
<td>1 × 10⁻⁶</td>
<td>Ar-H₂/H₂O</td>
<td>Oxidation</td>
<td>Fe-O</td>
<td></td>
<td></td>
<td>[Furukawa, 2004]</td>
</tr>
<tr>
<td>316FBR</td>
<td>550</td>
<td>800</td>
<td>1 × 10⁻⁸</td>
<td>Ar-H₂/H₂O</td>
<td>10</td>
<td>Oxidation</td>
<td>Fe-O</td>
<td></td>
<td>[Furukawa, 2004]</td>
</tr>
<tr>
<td>316FBR</td>
<td>550</td>
<td>2000</td>
<td>1 × 10⁻⁸</td>
<td>Ar-H₂/H₂O</td>
<td>20</td>
<td>Oxidation</td>
<td>Fe-O</td>
<td></td>
<td>[Furukawa, 2004]</td>
</tr>
<tr>
<td>316FBR</td>
<td>550</td>
<td>5000</td>
<td>1 × 10⁻⁸</td>
<td>Ar-H₂/H₂O</td>
<td></td>
<td>Dissolution</td>
<td>+ Cr₂O₃</td>
<td></td>
<td>[Furukawa, 2004]</td>
</tr>
<tr>
<td>316FBR</td>
<td>600</td>
<td>800, 2000</td>
<td>1 × 10⁻⁸</td>
<td>Ar-H₂/H₂O</td>
<td>Dissolution</td>
<td></td>
<td></td>
<td></td>
<td>[Furukawa, 2004]</td>
</tr>
<tr>
<td>316FBR</td>
<td>600</td>
<td>5000</td>
<td>1 × 10⁻⁸</td>
<td>Ar-H₂/H₂O</td>
<td>Dissolution</td>
<td>+ Cr₂O₃</td>
<td></td>
<td></td>
<td>[Furukawa, 2004]</td>
</tr>
<tr>
<td>316FBR</td>
<td>650</td>
<td>800, 2000, 5000</td>
<td>1 × 10⁻⁶</td>
<td>Ar-H₂/H₂O</td>
<td>Dissolution</td>
<td></td>
<td></td>
<td></td>
<td>[Furukawa, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>100</td>
<td>4 × 10⁻⁷</td>
<td>H₂/H₂O</td>
<td>5.0.004</td>
<td>Dissolution</td>
<td>-9</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>535</td>
<td>3000</td>
<td>3 × 10⁻⁷</td>
<td>H₂/H₂O</td>
<td>5.0.004</td>
<td>Oxidation</td>
<td>Oxide nodules</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>3000</td>
<td>4 × 10⁻⁷</td>
<td>H₂/H₂O</td>
<td>5.0.004</td>
<td>Dissolution</td>
<td>-46</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>535</td>
<td>500</td>
<td>8 × 10⁻⁵</td>
<td>H₂/H₂O</td>
<td>5.0.004</td>
<td>Oxidation</td>
<td></td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>Material</td>
<td>T (°C)</td>
<td>Time (hours)</td>
<td>([\text{O}]) (%wt.)</td>
<td>OCS</td>
<td>Surface sample/LBE volume ratio (cm(^2))</td>
<td>Oxide thickness/dissolution depth (microns)</td>
<td>Remark 1</td>
<td>Remark 2</td>
<td>Ref.</td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
<td>--------------</td>
<td>------------------</td>
<td>----------</td>
<td>------------------------------------------</td>
<td>--------------------------------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>500</td>
<td>(8 \times 10^{-6})</td>
<td>H(_2)/H(_2)O</td>
<td>5 / 0.004</td>
<td>9</td>
<td>Oxidation</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>500</td>
<td>(8 \times 10^{-6})</td>
<td>H(_2)/H(_2)O</td>
<td>5 / 0.004</td>
<td>-55</td>
<td>Dissolution</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>535</td>
<td>3000</td>
<td>(3 \times 10^{-6})</td>
<td>H(_2)/H(_2)O</td>
<td>5 / 0.004</td>
<td>-60</td>
<td>Dissolution</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>3000</td>
<td>(4 \times 10^{-6})</td>
<td>H(_2)/H(_2)O</td>
<td>5 / 0.004</td>
<td>-70</td>
<td>Dissolution</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>3000</td>
<td>(8 \times 10^{-3})</td>
<td>H(_2)/H(_2)O</td>
<td>5 / 0.004</td>
<td>-156</td>
<td>Dissolution</td>
<td></td>
<td>[Martin, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>450</td>
<td>3000</td>
<td>(6 \times 10^{-3})</td>
<td>H(_2)/H(_2)O</td>
<td>5 / 0.004</td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td>[Gómez, 2004]</td>
<td></td>
</tr>
<tr>
<td>316L-preox</td>
<td>450</td>
<td>3000</td>
<td>(6 \times 10^{-3})</td>
<td>H(_2)/H(_2)O</td>
<td>5 / 0.004</td>
<td>Oxidation</td>
<td>Oxide nodules</td>
<td></td>
<td>[Gómez, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>100</td>
<td>(4.7 \times 10^{-4})</td>
<td>Ar + H(_2)+ H(_2)O</td>
<td>9.7/0.035</td>
<td>8</td>
<td>Oxidation</td>
<td></td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>500</td>
<td>(4.7 \times 10^{-4})</td>
<td>Ar + H(_2)+ H(_2)O</td>
<td>9.7/0.035</td>
<td>27</td>
<td>Oxidation</td>
<td></td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>1500</td>
<td>(4.7 \times 10^{-4})</td>
<td>Ar + H(_2)+ H(_2)O</td>
<td>9.7/0.035</td>
<td>45</td>
<td>Oxidation</td>
<td></td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>100</td>
<td>(2 \times 10^{-3})</td>
<td>Ar-saturation</td>
<td>9.7/0.035</td>
<td>0.3</td>
<td>Oxidation</td>
<td>Oxide nodules 7</td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>500</td>
<td>(2 \times 10^{-3})</td>
<td>Ar-saturation</td>
<td>9.7/0.035</td>
<td>24</td>
<td>Oxidation</td>
<td></td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>1500</td>
<td>(2 \times 10^{-3})</td>
<td>Ar-saturation</td>
<td>9.7/0.035</td>
<td>15</td>
<td>Oxidation</td>
<td></td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>450</td>
<td>500</td>
<td>(3 \times 10^{-4})</td>
<td>Ar-saturation</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>450</td>
<td>100, 1500</td>
<td>(6 \times 10^{-4})</td>
<td>H(_2)/H(_2)O</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td></td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>100</td>
<td>(1.1 \times 10^{-4})</td>
<td>H(_2)/H(_2)O</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td></td>
<td></td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>1500</td>
<td>(1.1 \times 10^{-4})</td>
<td>H(_2)/H(_2)O</td>
<td>9.7/0.035</td>
<td>-83</td>
<td>Dissolution</td>
<td></td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>450</td>
<td>500</td>
<td>(1.1 \times 10^{-4})</td>
<td>Ar + H(_2)</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td>[Soler, 2004]</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>450</td>
<td>2400</td>
<td>(1.1 \times 10^{-4})</td>
<td>Ar + H(_2)</td>
<td>9.7/0.035</td>
<td>-25</td>
<td>Dissolution</td>
<td>Slight dissolution</td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>500</td>
<td>(1.1 \times 10^{-4})</td>
<td>Ar + H(_2)</td>
<td>9.7/0.035</td>
<td>-40</td>
<td>Dissolution</td>
<td>Coexistence of dissolution and oxidation</td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>1500</td>
<td>(1.1 \times 10^{-4})</td>
<td>Ar + H(_2)</td>
<td>9.7/0.035</td>
<td>-63</td>
<td>Dissolution</td>
<td></td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>300</td>
<td>1500</td>
<td>(1.85 \times 10^{-5})</td>
<td>Saturation</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>Thin</td>
<td></td>
<td>[Long Bin, 2003]</td>
</tr>
<tr>
<td>316L</td>
<td>400</td>
<td>1500</td>
<td>(1.41 \times 10^{-4})</td>
<td>Saturation</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>Thin</td>
<td></td>
<td>[Long Bin, 2003]</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>1500</td>
<td>(1.17 \times 10^{-4})</td>
<td>Saturation</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>Thin, Discontinuous and spongy</td>
<td></td>
<td>[Long Bin, 2003]</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>3000</td>
<td>(1.17 \times 10^{-4})</td>
<td>Saturation</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>Thin, Pb-Bi penetration.</td>
<td></td>
<td>[Long Bin, 2003]</td>
</tr>
<tr>
<td>316L</td>
<td>300</td>
<td>5000</td>
<td>(1.85 \times 10^{-5})</td>
<td>Saturation</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>Thin</td>
<td></td>
<td>[Long Bin, 2003]</td>
</tr>
<tr>
<td>316L</td>
<td>400</td>
<td>5000</td>
<td>(1.41 \times 10^{-4})</td>
<td>Saturation</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>Thin</td>
<td></td>
<td>[Long Bin, 2003]</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>5000</td>
<td>(1.17 \times 10^{-4})</td>
<td>Saturation</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>Thin, Pb-bi penetration deeper</td>
<td></td>
<td>[Long Bin, 2003]</td>
</tr>
<tr>
<td>316L</td>
<td>500</td>
<td>800</td>
<td>(1 \times 10^{-6})</td>
<td>H(_2)/H(_2)O</td>
<td>6</td>
<td>Oxidation</td>
<td>Oxide nodes</td>
<td></td>
<td>[Müller, 2004]</td>
</tr>
<tr>
<td>316L</td>
<td>500</td>
<td>2000</td>
<td>(1 \times 10^{-6})</td>
<td>H(_2)/H(_2)O</td>
<td>6</td>
<td>Oxidation</td>
<td>Oxide nodes</td>
<td></td>
<td>[Müller, 2004]</td>
</tr>
<tr>
<td>Material</td>
<td>T (°C)</td>
<td>Time (hours)</td>
<td>[O] (%wt.)</td>
<td>OCS</td>
<td>Surface sample/LBE volume ratio (cm²/l)</td>
<td>Oxide thickness/dissolution depth (microns)</td>
<td>Remark 1</td>
<td>Remark 2</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------</td>
<td>--------</td>
<td>--------------</td>
<td>------------</td>
<td>-----</td>
<td>----------------------------------------</td>
<td>---------------------------------------------</td>
<td>---------</td>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>316L</td>
<td>500</td>
<td>5000</td>
<td>1 x 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>6</td>
<td>Oxidation</td>
<td>Oxide nodes</td>
<td></td>
<td>Müller, 2004</td>
</tr>
<tr>
<td>316L</td>
<td>500</td>
<td>10000</td>
<td>1 x 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>-40</td>
<td>Oxidation</td>
<td>Coexistence with oxide layers</td>
<td></td>
<td>Müller, 2004</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>800</td>
<td>1 x 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>10-20</td>
<td>Oxidation</td>
<td>Air intake</td>
<td></td>
<td>Müller, 2004</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>2000</td>
<td>1 x 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>10-20</td>
<td>Oxidation</td>
<td>Air intake</td>
<td></td>
<td>Müller, 2004</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>5000</td>
<td>1 x 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>15</td>
<td>Oxidation</td>
<td>Pb-Bi penetration</td>
<td></td>
<td>Müller, 2004</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>10000</td>
<td>1 x 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>-200</td>
<td>Dissolution</td>
<td></td>
<td>Müller, 2004</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>800</td>
<td>1 x 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>5-10</td>
<td>Dissolution</td>
<td>Thin spinel</td>
<td></td>
<td>Müller, 2004</td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>2000</td>
<td>1 x 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>-20</td>
<td>Dissolution</td>
<td></td>
<td>Müller, 2004</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>5000</td>
<td>1 x 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>-20</td>
<td>Dissolution</td>
<td></td>
<td>Müller, 2004</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>10000</td>
<td>1 x 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>-180</td>
<td>Dissolution</td>
<td></td>
<td>Müller, 2004</td>
<td></td>
</tr>
<tr>
<td>316L*</td>
<td>450</td>
<td>550</td>
<td>3.14 x 10⁻⁴</td>
<td></td>
<td>&lt;3</td>
<td>Oxidation</td>
<td></td>
<td>Gnecco, 2004</td>
<td></td>
</tr>
<tr>
<td>316L*</td>
<td>550</td>
<td>550</td>
<td>Ar N60</td>
<td></td>
<td>7</td>
<td>Oxidation</td>
<td></td>
<td>Gnecco, 2004</td>
<td></td>
</tr>
<tr>
<td>316L*</td>
<td>600</td>
<td>550</td>
<td>Ar N60</td>
<td></td>
<td>20</td>
<td>Oxidation</td>
<td></td>
<td>Gnecco, 2004</td>
<td></td>
</tr>
<tr>
<td>316L*</td>
<td>350</td>
<td>1000</td>
<td>Ar N60</td>
<td></td>
<td>-</td>
<td>Oxidation</td>
<td></td>
<td>Gnecco, 2004</td>
<td></td>
</tr>
<tr>
<td>316L*</td>
<td>450</td>
<td>1000</td>
<td>Ar N60</td>
<td></td>
<td>3</td>
<td>Oxidation</td>
<td></td>
<td>Gnecco, 2004</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>1000</td>
<td>1.17 x 10⁻⁴</td>
<td></td>
<td>8</td>
<td>Oxidation</td>
<td></td>
<td>Gnecco, 2004</td>
<td></td>
</tr>
<tr>
<td>316L*</td>
<td>600</td>
<td>1000</td>
<td>Ar N60</td>
<td></td>
<td>&lt;20</td>
<td>Oxidation</td>
<td></td>
<td>Gnecco, 2004</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>550</td>
<td>3.9 x 10⁻⁸</td>
<td>Ar + 5%H₂</td>
<td>-50</td>
<td>Dissolution</td>
<td></td>
<td>Gnecco, 2004</td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>550</td>
<td>100</td>
<td>4 x 10⁻⁷</td>
<td>H₂/H₂O</td>
<td>5/0.004</td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td></td>
<td>Martin, 2004</td>
</tr>
<tr>
<td>304L</td>
<td>535</td>
<td>3000</td>
<td>3 x 10⁻⁷</td>
<td>H₂/H₂O</td>
<td>5/0.004</td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td></td>
<td>Martin, 2004</td>
</tr>
<tr>
<td>304L</td>
<td>550</td>
<td>3000</td>
<td>4 x 10⁻⁷</td>
<td>H₂/H₂O</td>
<td>5/0.004</td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td></td>
<td>Martin, 2004</td>
</tr>
<tr>
<td>304L</td>
<td>550</td>
<td>500</td>
<td>8 x 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5/0.004</td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td></td>
<td>Martin, 2004</td>
</tr>
<tr>
<td>304L</td>
<td>550</td>
<td>500</td>
<td>8 x 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5/0.004</td>
<td>Oxidation</td>
<td>Oxide nodules</td>
<td></td>
<td>Martin, 2004</td>
</tr>
<tr>
<td>304L</td>
<td>600</td>
<td>500</td>
<td>8 x 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5/0.004</td>
<td>Oxidation</td>
<td>Oxide nodules</td>
<td></td>
<td>Martin, 2004</td>
</tr>
<tr>
<td>304L</td>
<td>535</td>
<td>3000</td>
<td>3 x 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5/0.004</td>
<td>Oxidation</td>
<td>-35</td>
<td></td>
<td>Martin, 2004</td>
</tr>
<tr>
<td>304L</td>
<td>550</td>
<td>3000</td>
<td>4 x 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5/0.004</td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td></td>
<td>Martin, 2004</td>
</tr>
<tr>
<td>304L</td>
<td>600</td>
<td>3000</td>
<td>8 x 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5/0.004</td>
<td>Oxidation</td>
<td>Oxide nodules</td>
<td></td>
<td>Martin, 2004</td>
</tr>
<tr>
<td>304L</td>
<td>450</td>
<td>3000</td>
<td>6 x 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5/0.004</td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td></td>
<td>Gomez, 2004</td>
</tr>
<tr>
<td>304L-preox</td>
<td>450</td>
<td>3000</td>
<td>6 x 10⁻⁶</td>
<td>H₂/H₂O</td>
<td>5/0.004</td>
<td>Oxidation</td>
<td>Cr oxide</td>
<td></td>
<td>Gomez, 2004</td>
</tr>
<tr>
<td>304L</td>
<td>600</td>
<td>100</td>
<td>4.7 x 10⁻⁴</td>
<td>Ar + H₂ + H₂O</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>0.5</td>
<td>Oxide nodules</td>
<td>Soler, 2004</td>
</tr>
<tr>
<td>304L</td>
<td>600</td>
<td>500, 1500</td>
<td>4.7 x 10⁻⁴</td>
<td>Ar + H₂ + H₂O</td>
<td>9.7/0.035</td>
<td>Oxidation</td>
<td>0.5</td>
<td>Oxide nodules</td>
<td>Soler, 2004</td>
</tr>
</tbody>
</table>
Table 6.3.4. Fe-Cr-Ni steels in stagnant LBE (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Time (hours)</th>
<th>[O] (%wt.)</th>
<th>OCS</th>
<th>Surface sample/LBE volume ratio (cm²/l)</th>
<th>Oxide thickness/dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>600</td>
<td>100</td>
<td>2 × 10⁻²</td>
<td>Ar-saturation</td>
<td>9.7/0.035</td>
<td>0.2</td>
<td>Oxidation</td>
<td></td>
<td>[Soler, 2004]</td>
</tr>
<tr>
<td>304L</td>
<td>600</td>
<td>500</td>
<td>2 × 10⁻³</td>
<td>Ar-saturation</td>
<td>9.7/0.035</td>
<td>Oxide nodules 17</td>
<td>[Soler, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>600</td>
<td>1500</td>
<td>2 × 10⁻³</td>
<td>Ar-saturation</td>
<td>9.7/0.035</td>
<td>Slight dissolution</td>
<td>[Soler, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>450</td>
<td>500</td>
<td>3 × 10⁻⁴</td>
<td>Ar-saturation</td>
<td>9.7/0.035</td>
<td>Oxide Cr oxide</td>
<td>[Soler, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>450</td>
<td>100, 1500</td>
<td>6 × 10⁻³</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>Oxidation Cr oxide</td>
<td>[Soler, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>600</td>
<td>100</td>
<td>1.1 × 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>Dissolution</td>
<td>[Soler, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>600</td>
<td>1500</td>
<td>1.1 × 10⁻⁸</td>
<td>H₂/H₂O</td>
<td>9.7/0.035</td>
<td>Dissolution</td>
<td>[Soler, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>450</td>
<td>500</td>
<td>1.1 × 10⁻⁸</td>
<td>Ar + H₂</td>
<td>9.7/0.035</td>
<td>Oxidation Cr oxidation</td>
<td>[Soler, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>450</td>
<td>2400</td>
<td>1.1 × 10⁻⁸</td>
<td>Ar + H₂</td>
<td>9.7/0.035</td>
<td>Slight dissolution</td>
<td>[Soler, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>600</td>
<td>500</td>
<td>1.1 × 10⁻⁸</td>
<td>Ar + H₂</td>
<td>9.7/0.035</td>
<td>Slight dissolution</td>
<td>[Soler, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>600</td>
<td>1500</td>
<td>1.1 × 10⁻⁸</td>
<td>Ar + H₂</td>
<td>9.7/0.035</td>
<td>Dissolution</td>
<td>[Soler, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>JPCA</td>
<td>450</td>
<td>3000</td>
<td>3.2 × 10⁻⁴</td>
<td>Ar-saturation</td>
<td>21.6/0.7</td>
<td>Oxidation</td>
<td>[Kurata, 2005]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316ss</td>
<td>450</td>
<td>3000</td>
<td>3.2 × 10⁻⁴</td>
<td>Ar-saturation</td>
<td>21.6/0.7</td>
<td>Oxidation</td>
<td>[Kurata, 2005]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SX</td>
<td>450</td>
<td>3000</td>
<td>3.2 × 10⁻⁴</td>
<td>Ar-saturation</td>
<td>21.6/0.7</td>
<td>Oxidation</td>
<td>[Kurata, 2005]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>JPCA</td>
<td>550</td>
<td>3000</td>
<td>1.2 × 10⁻³</td>
<td>Ar-saturation</td>
<td>21.6/0.7</td>
<td>Dissolution</td>
<td>[Kurata, 2005]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316ss</td>
<td>550</td>
<td>3000</td>
<td>1.2 × 10⁻³</td>
<td>Ar-saturation</td>
<td>21.6/0.7</td>
<td>Dissolution</td>
<td>[Kurata, 2005]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SX</td>
<td>550</td>
<td>3000</td>
<td>1.2 × 10⁻³</td>
<td>Ar-saturation</td>
<td>21.6/0.7</td>
<td>Dissolution</td>
<td>[Kurata, 2005]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Not clarified enough (oxygen content information missed).
<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>ΔT</th>
<th>Time (hours)</th>
<th>[O] (%wt.)</th>
<th>OCS</th>
<th>Loop</th>
<th>Volume LBE (l)</th>
<th>Flow rate (m/s)</th>
<th>Oxide thickness/dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>F82H</td>
<td>500</td>
<td>100</td>
<td>340, 1030</td>
<td>6 × 10⁻⁶</td>
<td>Ar + 10 ppm</td>
<td>CIRCO</td>
<td>1.2</td>
<td>0.06</td>
<td>2.5-3.5</td>
<td>Oxidation</td>
<td>Exposure from beginning of operation</td>
<td>[Gómez, 2001]</td>
</tr>
<tr>
<td>F82H</td>
<td>500</td>
<td>100</td>
<td>3000</td>
<td>6 × 10⁻⁶</td>
<td>Ar + 10 ppm</td>
<td>CIRCO</td>
<td>1.2</td>
<td>0.06</td>
<td>20</td>
<td>Oxidation</td>
<td>Exposure from beginning of operation</td>
<td>[Gómez, 2001]</td>
</tr>
<tr>
<td>F82H</td>
<td>500</td>
<td>100</td>
<td>690</td>
<td>6 × 10⁻⁶</td>
<td>Ar + 10 ppm</td>
<td>CIRCO</td>
<td>1.2</td>
<td>0.06</td>
<td>-50</td>
<td>Dissolution</td>
<td>Intermediate time. Specimens inserted after 340 h from starting.</td>
<td>[Gómez, 2001]</td>
</tr>
<tr>
<td>F82H</td>
<td>500</td>
<td>100</td>
<td>960</td>
<td>6 × 10⁻⁶</td>
<td>Ar + 10 ppm</td>
<td>CIRCO</td>
<td>1.2</td>
<td>0.06</td>
<td>&lt;1</td>
<td>Dissolution</td>
<td>Intermediate time. Specimens inserted after 1030 h from starting.</td>
<td>[Gómez, 2001]</td>
</tr>
<tr>
<td>F82H</td>
<td>500</td>
<td>100</td>
<td>1992</td>
<td>6 × 10⁻⁶</td>
<td>Ar + 10 ppm</td>
<td>CIRCO</td>
<td>1.2</td>
<td>0.06</td>
<td>-140</td>
<td>Dissolution</td>
<td>Intermediate time. Specimens inserted after 1030 h from starting.</td>
<td>[Gómez, 2001]</td>
</tr>
<tr>
<td>F82H</td>
<td>500</td>
<td>100</td>
<td>1032</td>
<td>6 × 10⁻⁶</td>
<td>Ar + 10 ppm</td>
<td>CIRCO</td>
<td>1.2</td>
<td>0.06</td>
<td>&lt;1</td>
<td>Dissolution</td>
<td>Intermediate time. Specimens inserted after 1990 h from starting.</td>
<td>[Gómez, 2001]</td>
</tr>
<tr>
<td>F82H</td>
<td>550</td>
<td>100</td>
<td>1000</td>
<td>3.6 × 10⁻⁷</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td></td>
<td>2</td>
<td></td>
<td>Dissolution Erosion damage</td>
<td></td>
<td></td>
<td>[Takahashi, 2002]</td>
</tr>
<tr>
<td>F82H</td>
<td>550</td>
<td>150</td>
<td>1000</td>
<td>2 × 10⁻⁹</td>
<td>H₂/H₂O</td>
<td></td>
<td>22</td>
<td>2</td>
<td>-22</td>
<td>Dissolution</td>
<td>Severe erosion</td>
<td>[Kondo, 2005]</td>
</tr>
<tr>
<td>STBA28</td>
<td>550</td>
<td>100</td>
<td>1000</td>
<td>3.6 × 10⁻⁷</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td></td>
<td>2</td>
<td></td>
<td>-20</td>
<td>Dissolution</td>
<td></td>
<td>[Takahashi, 2002]</td>
</tr>
<tr>
<td>STBA28</td>
<td>550</td>
<td>150</td>
<td>1000</td>
<td>2 × 10⁻⁹</td>
<td>H₂/H₂O</td>
<td></td>
<td>22</td>
<td>2</td>
<td>-20</td>
<td>Dissolution</td>
<td>No erosion</td>
<td>[Kondo, 2005]</td>
</tr>
<tr>
<td>T91</td>
<td>300</td>
<td>170</td>
<td>1116, 2000, 3116</td>
<td>1-2 × 10⁻⁶</td>
<td>He-20%H₂PbO</td>
<td>Cu-1 M (IPPE) Preoxidated</td>
<td>60</td>
<td>2</td>
<td>Dissolution</td>
<td>Heterogeneous oxidation</td>
<td>[Barbier, 2001]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>470</td>
<td>170</td>
<td>1116</td>
<td>1-2 × 10⁻⁶</td>
<td>He-20%H₂PbO</td>
<td>Cu-1 M (IPPE) Preoxidated</td>
<td>60</td>
<td>2</td>
<td>11</td>
<td>Oxidation</td>
<td>Weight gain (mg/mm²): 0.35</td>
<td>[Barbier, 2001]</td>
</tr>
<tr>
<td>T91</td>
<td>470</td>
<td>2000</td>
<td>1-2 × 10⁻⁶</td>
<td>He-20%H₂PbO</td>
<td>Cu-1 M (IPPE) Preoxidated</td>
<td>60</td>
<td>2</td>
<td>14</td>
<td>Oxidation</td>
<td>Weight gain (mg/mm²): 0.5</td>
<td>[Barbier, 2001]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>470</td>
<td>3116</td>
<td>1-2 × 10⁻⁶</td>
<td>He-20%H₂PbO</td>
<td>Cu-1 M (IPPE) Preoxidated</td>
<td>60</td>
<td>2</td>
<td>16</td>
<td>Oxidation</td>
<td>Weight gain (mg/mm²): 0.45</td>
<td>[Barbier, 2001]</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>400</td>
<td>1500</td>
<td>3.1 × 10⁻¹⁰, 7.3 × 10⁻⁸</td>
<td>Mg + Ar/H₂</td>
<td>LECOR</td>
<td></td>
<td>60</td>
<td>1</td>
<td>Dissolution</td>
<td>2.9 × 10⁻³ μm/h</td>
<td>[Fazio, 2003]</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.3.5. Fe-Cr steels in flowing LBE (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>ΔT</th>
<th>Time (hours)</th>
<th>[O] (%wt.)</th>
<th>OCS</th>
<th>Loop</th>
<th>Volume LBE (l)</th>
<th>Flow rate (m/s)</th>
<th>Oxide thickness/dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91</td>
<td>400</td>
<td>550</td>
<td>1000</td>
<td>1 x 10^-7</td>
<td>LECOR</td>
<td>1</td>
<td>-1.97</td>
<td>Dissolution</td>
<td>Weight loss (mg/mm²): 0.0375</td>
<td>[Aiello, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>400</td>
<td>450</td>
<td>1000</td>
<td>1 x 10^-9</td>
<td>LECOR</td>
<td>1</td>
<td>-2.38</td>
<td>Dissolution</td>
<td>Weight loss (mg/mm²): 0.184</td>
<td>[Aiello, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>400</td>
<td>3000</td>
<td>10^-6-10^-3</td>
<td>CHEOPE III</td>
<td>1</td>
<td>2.4</td>
<td>Oxidation</td>
<td>Weight gain(mg/mm²): 3 x 10^-4</td>
<td>[Aiello, 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STBA26</td>
<td>550</td>
<td>959</td>
<td>1000</td>
<td>3.6 x 10^-7</td>
<td>H₂/HeO = 0.12-2.2</td>
<td>2</td>
<td>-20</td>
<td>Dissolution</td>
<td>Erosion damage</td>
<td>[Takahashi, 2002]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>STBA26</td>
<td>550</td>
<td>1000</td>
<td>2 x 10^-9</td>
<td>H₂/HeO = 0.12-2.2</td>
<td>22</td>
<td>2</td>
<td>Dissolution</td>
<td>Severe erosion</td>
<td>[Kondo, 2005]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optifer IVc</td>
<td>300</td>
<td>170</td>
<td>1116</td>
<td>1-2 x 10^-6</td>
<td>He-20%H₂PbO</td>
<td>Cu-1M(IPPE)Preoxidated</td>
<td>60</td>
<td>2</td>
<td>Heterogeneous oxidation. Weight gain (mg/mm²): 0.6</td>
<td>[Barbier, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optifer IVc</td>
<td>470</td>
<td>170</td>
<td>1116</td>
<td>1-2 x 10^-6</td>
<td>He-20%H₂PbO</td>
<td>Cu-1M(IPPE)Preoxidated</td>
<td>60</td>
<td>2</td>
<td>Oxidation</td>
<td>[Barbier, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optifer IVc</td>
<td>300</td>
<td>2000,3116</td>
<td>1-2 x 10^-6</td>
<td>He-20%H₂PbO</td>
<td>Cu-1M(IPPE)Preoxidated</td>
<td>60</td>
<td>2</td>
<td>Heterogeneous oxidation</td>
<td>[Barbier, 2001]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optifer IVc</td>
<td>470</td>
<td>170</td>
<td>2000</td>
<td>1-2 x 10^-6</td>
<td>He-20%H₂PbO</td>
<td>Cu-1M(IPPE)Preoxidated</td>
<td>60</td>
<td>2</td>
<td>Oxidation</td>
<td>Weight gain(mg/mm²): 0.7</td>
<td>[Barbier, 2001]</td>
<td></td>
</tr>
<tr>
<td>Optifer IVc</td>
<td>470</td>
<td>170</td>
<td>3116</td>
<td>1-2 x 10^-6</td>
<td>He-20%H₂PbO</td>
<td>Cu-1M(IPPE)Preoxidated</td>
<td>60</td>
<td>2</td>
<td>Oxidation</td>
<td>[Barbier, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>420</td>
<td>180</td>
<td>2000</td>
<td>1 x 10^-6</td>
<td>ArH₂ + PbO</td>
<td>IPPE</td>
<td>60</td>
<td>1.3</td>
<td>Oxidation</td>
<td>[Müller, 2002]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>420</td>
<td>4000</td>
<td>1 x 10^-6</td>
<td>ArH₂ + PbO</td>
<td>IPPE</td>
<td>60</td>
<td>1.3</td>
<td>Oxidation</td>
<td>[Müller, 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>550</td>
<td>2000</td>
<td>1 x 10^-6</td>
<td>ArH₂ + PbO</td>
<td>Prometey</td>
<td>60</td>
<td>0.5</td>
<td>Oxidation</td>
<td>Spalls</td>
<td>[Müller, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manet II</td>
<td>550</td>
<td>4000</td>
<td>1 x 10^-6</td>
<td>ArH₂ + PbO</td>
<td>Prometey</td>
<td>60</td>
<td>0.5</td>
<td>Oxidation</td>
<td>New oxide</td>
<td>[Müller, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODS</td>
<td>550</td>
<td>7200</td>
<td>1 x 10^-6</td>
<td>ArH₂ + PbO</td>
<td>Prometey</td>
<td>60</td>
<td>0.5</td>
<td>Oxidation</td>
<td>New oxide</td>
<td>[Müller, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ODS</td>
<td>550</td>
<td>1000</td>
<td>3.6 x 10^-7</td>
<td>H₂/HeO = 0.12-2.2</td>
<td>2</td>
<td>2</td>
<td>Dissolution</td>
<td>No erosion</td>
<td>[Takahashi, 2002]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6.3.5. Fe-Cr steels in flowing LBE (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>ΔT</th>
<th>Time (hours)</th>
<th>([O]) (% wt.)</th>
<th>OCS</th>
<th>Loop</th>
<th>Volume LBE (l)</th>
<th>Flow rate (m/s)</th>
<th>Oxide thickness/ dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP823</td>
<td>300</td>
<td>170</td>
<td>1116, 2000, 3116</td>
<td>1-2 × 10⁻⁶</td>
<td>He-20%H₂</td>
<td>Cu-1M (IPPE)</td>
<td>Preoxidated</td>
<td>60</td>
<td>2</td>
<td>Heterogeneous oxidation</td>
<td></td>
<td>[Barbier, 2001]</td>
</tr>
<tr>
<td>EP823</td>
<td>470</td>
<td>170</td>
<td>1116</td>
<td>1-2 × 10⁻⁶</td>
<td>He-20%H₂</td>
<td>Cu-1M (IPPE)</td>
<td>Preoxidated</td>
<td>60</td>
<td>2</td>
<td>Oxidation</td>
<td>Weight gain (mg/mm²): 0.25</td>
<td>[Barbier, 2001]</td>
</tr>
<tr>
<td>EP823</td>
<td>470</td>
<td>170</td>
<td>2000</td>
<td>1-2 × 10⁻⁶</td>
<td>He-20%H₂</td>
<td>Cu-1M (IPPE)</td>
<td>Preoxidated</td>
<td>60</td>
<td>2</td>
<td>Oxidation</td>
<td>Weight gain (mg/mm²): 0.25</td>
<td>[Barbier, 2001]</td>
</tr>
<tr>
<td>EP823</td>
<td>470</td>
<td>170</td>
<td>3116</td>
<td>1-2 × 10⁻⁶</td>
<td>He-20%H₂</td>
<td>Cu-1M (IPPE)</td>
<td>Preoxidated</td>
<td>60</td>
<td>2</td>
<td>Oxidation</td>
<td>Weight gain (mg/mm²): 0.25</td>
<td>[Barbier, 2001]</td>
</tr>
<tr>
<td>EP823</td>
<td>350</td>
<td>700</td>
<td>4 × 10⁻⁶</td>
<td></td>
<td></td>
<td>CU-2</td>
<td>IPPE</td>
<td>2</td>
<td>Thin</td>
<td>[Benamati, 2002]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP823</td>
<td>450</td>
<td>700</td>
<td>4 × 10⁻⁶</td>
<td></td>
<td></td>
<td>CU-2</td>
<td>IPPE</td>
<td>2</td>
<td>0.2-6.5</td>
<td>[Benamati, 2002]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP823</td>
<td>550</td>
<td>700</td>
<td>4 × 10⁻⁶</td>
<td></td>
<td></td>
<td>CU-2</td>
<td>IPPE</td>
<td>2</td>
<td>0.6-11.5</td>
<td>[Benamati, 2002]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP823 rod</td>
<td>460</td>
<td>300</td>
<td>1000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M</td>
<td>IPPE</td>
<td>60</td>
<td>1.9</td>
<td>0</td>
<td>Weight gain (mg/mm²): 0.003</td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>EP823 rod</td>
<td>550</td>
<td>300</td>
<td>1000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M</td>
<td>IPPE</td>
<td>60</td>
<td>1.9</td>
<td>1</td>
<td>Weight loss (mg/mm²): 0.001</td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>EP823 rod</td>
<td>460</td>
<td>300</td>
<td>2000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M</td>
<td>IPPE</td>
<td>60</td>
<td>1.9</td>
<td>7</td>
<td>Weight gain (mg/mm²): 0.003</td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>EP823 rod</td>
<td>550</td>
<td>300</td>
<td>2000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M</td>
<td>IPPE</td>
<td>60</td>
<td>1.9</td>
<td>2</td>
<td>Weight gain (mg/mm²): 0.001</td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>EP823 rod</td>
<td>460</td>
<td>300</td>
<td>3000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M</td>
<td>IPPE</td>
<td>60</td>
<td>1.9</td>
<td>6</td>
<td>Oxidation</td>
<td>Weight gain (mg/mm²): 0.008</td>
</tr>
<tr>
<td>EP823 rod</td>
<td>550</td>
<td>300</td>
<td>3000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M</td>
<td>IPPE</td>
<td>60</td>
<td>1.9</td>
<td>11</td>
<td>Oxidation</td>
<td>Weight gain (mg/mm²): 0.00</td>
</tr>
<tr>
<td>HT-9 tube</td>
<td>460</td>
<td>300</td>
<td>1000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M</td>
<td>IPPE</td>
<td>60</td>
<td>1.9</td>
<td>5</td>
<td>Weight gain (mg/mm²): 0.002</td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>HT-9 tube</td>
<td>550</td>
<td>300</td>
<td>1000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M</td>
<td>IPPE</td>
<td>60</td>
<td>1.9</td>
<td>20</td>
<td>Weight gain (mg/mm²): 0.003</td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>HT-9 tube</td>
<td>460</td>
<td>300</td>
<td>2000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M</td>
<td>IPPE</td>
<td>60</td>
<td>1.9</td>
<td>13</td>
<td>Weight gain (mg/mm²): 0.025</td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>HT-9 tube</td>
<td>550</td>
<td>300</td>
<td>2000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M</td>
<td>IPPE</td>
<td>60</td>
<td>1.9</td>
<td>34</td>
<td>Weight gain (mg/mm²): 0.04</td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>HT-9 tube</td>
<td>460</td>
<td>300</td>
<td>3000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M</td>
<td>IPPE</td>
<td>60</td>
<td>1.9</td>
<td>15</td>
<td>Oxidation</td>
<td>Weight gain (mg/mm²): 0.026</td>
</tr>
<tr>
<td>Material</td>
<td>T (°C)</td>
<td>ΔT</td>
<td>Time (hours)</td>
<td>[O] (%wt.)</td>
<td>OCS</td>
<td>Loop</td>
<td>Volume LBE (l)</td>
<td>Flow rate (m/s)</td>
<td>Oxide thickness/dissolution depth (microns)</td>
<td>Remark 1</td>
<td>Remark 2</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------------</td>
<td>-------</td>
<td>----</td>
<td>-------------</td>
<td>------------</td>
<td>---------</td>
<td>------------</td>
<td>----------------</td>
<td>----------------</td>
<td>---------------------------------------------</td>
<td>-----------------------------</td>
<td>----------------</td>
<td>--------</td>
</tr>
<tr>
<td>HT-9 tube</td>
<td>550</td>
<td>300</td>
<td>3000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M-IPPE</td>
<td>60</td>
<td>1.9</td>
<td>25</td>
<td>Oxidation</td>
<td>Weight loss: 0.004</td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>SCM420</td>
<td>550</td>
<td>959</td>
<td>5 × 10⁻³</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Weight loss: 38</td>
<td></td>
<td>[Takahashi, 2002]</td>
</tr>
<tr>
<td>SCM420</td>
<td>550</td>
<td>1000</td>
<td>3.6 × 10⁻⁷</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>-40</td>
<td>Erosion damage</td>
<td></td>
<td>[Takahashi, 2002]</td>
</tr>
<tr>
<td>SCM420</td>
<td>550</td>
<td>150</td>
<td>1000</td>
<td>2 × 10⁻⁹</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>22</td>
<td></td>
<td></td>
<td>-40</td>
<td>Dissolution</td>
<td>Severe erosion</td>
<td></td>
</tr>
<tr>
<td>SUS405</td>
<td>550</td>
<td>959</td>
<td>5 × 10⁻³</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Weight loss: 11</td>
<td></td>
<td>[Kondo, 2005]</td>
</tr>
<tr>
<td>SUS430</td>
<td>550</td>
<td>959</td>
<td>5 × 10⁻³</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Weight loss: 9</td>
<td></td>
<td>[Takahashi, 2002]</td>
</tr>
<tr>
<td>NF616</td>
<td>550</td>
<td>150</td>
<td>1000</td>
<td>2 × 10⁻⁹</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>22</td>
<td></td>
<td></td>
<td>-15</td>
<td>Dissolution</td>
<td>No erosion</td>
<td>[Kondo, 2005]</td>
</tr>
<tr>
<td>NF616</td>
<td>550</td>
<td>1000</td>
<td>3.6 × 10⁻⁷</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Weight loss: 22</td>
<td></td>
<td>[Takahashi, 2002]</td>
</tr>
<tr>
<td>HCM12</td>
<td>550</td>
<td>150</td>
<td>1000</td>
<td>2 × 10⁻⁹</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>22</td>
<td></td>
<td></td>
<td>-21</td>
<td>Dissolution</td>
<td>Crack-like erosion</td>
<td>[Kondo, 2005]</td>
</tr>
<tr>
<td>HCM12</td>
<td>550</td>
<td>1000</td>
<td>3.6 × 10⁻⁷</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Erosion damage (crack)</td>
<td></td>
<td>[Kondo, 2005]</td>
</tr>
<tr>
<td>HCM12A</td>
<td>550</td>
<td>150</td>
<td>1000</td>
<td>2 × 10⁻⁹</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>22</td>
<td></td>
<td></td>
<td>-15</td>
<td>Dissolution</td>
<td>No erosion</td>
<td>[Kondo, 2005]</td>
</tr>
<tr>
<td>HCM12A</td>
<td>550</td>
<td>1000</td>
<td>3.6 × 10⁻⁷</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Weight loss: 22</td>
<td></td>
<td>[Takahashi, 2002]</td>
</tr>
<tr>
<td>T-410 rod</td>
<td>460</td>
<td>300</td>
<td>1000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M-IPPE</td>
<td>60</td>
<td>1.9</td>
<td>6</td>
<td>Local corrosion more severe. No surface treatment.</td>
<td></td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>T-410 rod</td>
<td>550</td>
<td>300</td>
<td>1000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M-IPPE</td>
<td>60</td>
<td>1.9</td>
<td>15</td>
<td>Local corrosion more severe. No surface treatment.</td>
<td></td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>T-410 rod</td>
<td>460</td>
<td>300</td>
<td>2000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M-IPPE</td>
<td>60</td>
<td>1.9</td>
<td>13</td>
<td>Local corrosion more severe. No surface treatment.</td>
<td></td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>T-410 rod</td>
<td>550</td>
<td>300</td>
<td>2000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M-IPPE</td>
<td>60</td>
<td>1.9</td>
<td>24</td>
<td>Local corrosion more severe. No surface treatment.</td>
<td></td>
<td>[Li, 2001]</td>
</tr>
</tbody>
</table>
### Table 6.3.5. Fe-Cr steels in flowing LBE (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>ΔT (°C)</th>
<th>Time (hours)</th>
<th>[O] (%wt.)</th>
<th>OCS</th>
<th>Loop</th>
<th>Volume LBE (l)</th>
<th>Flow rate (m/s)</th>
<th>Oxide thickness/ dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-410 rod</td>
<td>460</td>
<td>300</td>
<td>3000</td>
<td>3-5 × 10^-6</td>
<td>CU-1M-IPPE</td>
<td></td>
<td>60</td>
<td>1.9</td>
<td>13</td>
<td>Dissolution</td>
<td>Local corrosion more severe. No surface treatment.</td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>T-410 rod</td>
<td>550</td>
<td>300</td>
<td>3000</td>
<td>3-5 × 10^-6</td>
<td>CU-1M-IPPE</td>
<td></td>
<td>60</td>
<td>1.9</td>
<td>19</td>
<td>Dissolution</td>
<td>Local corrosion more severe. No surface treatment.</td>
<td>[Li, 2001]</td>
</tr>
</tbody>
</table>
### Table 6.3.6. Fe-Cr-Ni steels in flowing LBE

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>ΔT</th>
<th>Time (hours)</th>
<th>[O] (%wt.)</th>
<th>OCS</th>
<th>Loop</th>
<th>LBE volume (litres)</th>
<th>Flow rate (m/s)</th>
<th>Oxide thickness/dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-9 tube</td>
<td>460</td>
<td>300</td>
<td>1000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>0</td>
<td>Weight gain (mg/mm²): 0.00</td>
<td></td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>D-9 tube</td>
<td>550</td>
<td>300</td>
<td>1000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>12</td>
<td>Weight gain (mg/mm²): 0.009</td>
<td></td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>D-9 tube</td>
<td>460</td>
<td>300</td>
<td>2000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>5</td>
<td>Weight gain (mg/mm²): 0.002</td>
<td></td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>D-9 tube</td>
<td>550</td>
<td>300</td>
<td>2000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>26</td>
<td>Weight gain (mg/mm²): 0.013</td>
<td></td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>D-9 tube</td>
<td>460</td>
<td>300</td>
<td>3000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>4</td>
<td>Weight gain (mg/mm²): 0.006</td>
<td></td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>D-9 tube</td>
<td>550</td>
<td>300</td>
<td>3000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>24</td>
<td>Weight gain (mg/mm²): 0.002</td>
<td></td>
<td>[Li, 2001]</td>
</tr>
<tr>
<td>1.4970</td>
<td>300</td>
<td>170</td>
<td>1116, 2000</td>
<td>3-5 × 10⁻⁶</td>
<td></td>
<td>Promoted PbO</td>
<td>60</td>
<td>2</td>
<td>Weight gain: 0.01</td>
<td></td>
<td></td>
<td>[Barbier, 2001]</td>
</tr>
<tr>
<td>1.4970</td>
<td>470</td>
<td>170</td>
<td>1116</td>
<td>1-2 × 10⁻⁶</td>
<td></td>
<td>Cu-1M (IPPE) Preoxidated</td>
<td>60</td>
<td>2</td>
<td>Weight gain: 0.04</td>
<td></td>
<td></td>
<td>[Barbier, 2001]</td>
</tr>
<tr>
<td>1.4970</td>
<td>470</td>
<td>170</td>
<td>2000</td>
<td>1-2 × 10⁻⁶</td>
<td></td>
<td>Cu-1M (IPPE) Preoxidated</td>
<td>60</td>
<td>2</td>
<td>&lt;1 Dissolution</td>
<td></td>
<td></td>
<td>[Barbier, 2001]</td>
</tr>
<tr>
<td>1.4970</td>
<td>300</td>
<td>170</td>
<td>3116</td>
<td>1-2 × 10⁻⁶</td>
<td></td>
<td>Cu-1M (IPPE) Preoxidated</td>
<td>60</td>
<td>2</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td>[Barbier, 2001]</td>
</tr>
<tr>
<td>1.4970</td>
<td>470</td>
<td>170</td>
<td>3116</td>
<td>1-2 × 10⁻⁶</td>
<td></td>
<td>Cu-1M (IPPE) Preoxidated</td>
<td>60</td>
<td>2</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td>[Barbier, 2001]</td>
</tr>
<tr>
<td>1.4970</td>
<td>420</td>
<td>180</td>
<td>2000, 4000</td>
<td>1 × 10⁻⁶</td>
<td></td>
<td>IPPE</td>
<td>60</td>
<td>1.3</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td>[Müller, 2002]</td>
</tr>
<tr>
<td>1.4970</td>
<td>550</td>
<td>2000</td>
<td>1 × 10⁻⁶</td>
<td></td>
<td>Promoted</td>
<td>60</td>
<td>0.5</td>
<td>30</td>
<td>Nodules</td>
<td></td>
<td>[Müller, 2002]</td>
<td></td>
</tr>
<tr>
<td>1.4970</td>
<td>550</td>
<td>4300</td>
<td>1 × 10⁻⁶</td>
<td></td>
<td>ArH₃ + PbO</td>
<td>60</td>
<td>0.5</td>
<td>15</td>
<td>Pb-Bi infiltration</td>
<td></td>
<td>[Müller, 2004]</td>
<td></td>
</tr>
<tr>
<td>1.4970</td>
<td>550</td>
<td>7200</td>
<td>1 × 10⁻⁶</td>
<td></td>
<td>ArH₃ + PbO</td>
<td>60</td>
<td>0.5</td>
<td>15 + 15</td>
<td>No LBE infiltration and growing of new oxide layer underneath</td>
<td></td>
<td>[Müller, 2004]</td>
<td></td>
</tr>
<tr>
<td>1.4970</td>
<td>600</td>
<td>180</td>
<td>2000</td>
<td>1 × 10⁻⁶</td>
<td></td>
<td>IPPE</td>
<td>60</td>
<td>1.3</td>
<td>30</td>
<td>Nodules</td>
<td></td>
<td>[Müller, 2002]</td>
</tr>
<tr>
<td>1.4970</td>
<td>600</td>
<td>4000</td>
<td>1 × 10⁻⁶</td>
<td></td>
<td>ArH₃ + PbO</td>
<td>60</td>
<td>1.3</td>
<td>-100 Dissolution</td>
<td></td>
<td></td>
<td>[Müller, 2004]</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>420</td>
<td>180</td>
<td>2000, 4000</td>
<td>1 × 10⁻⁶</td>
<td></td>
<td>IPPE</td>
<td>60</td>
<td>1.3</td>
<td>&lt;1</td>
<td>Nodules</td>
<td></td>
<td>[Müller, 2002]</td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>2000</td>
<td>1 × 10⁻⁶</td>
<td></td>
<td>Promoted</td>
<td>60</td>
<td>0.5</td>
<td>&lt;1</td>
<td>Oxidation</td>
<td></td>
<td>[Müller, 2002]</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.3.6. Fe-Cr-Ni steels in flowing LBE (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>ΔT</th>
<th>Time (hours)</th>
<th>[O] (%) wt.</th>
<th>OCS</th>
<th>Loop</th>
<th>LBE volume (litres)</th>
<th>Flow rate (m/s)</th>
<th>Oxide thickness/dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>550</td>
<td>1</td>
<td>4000</td>
<td>$1 \times 10^{-6}$ ArH$_2$ + PbO</td>
<td>Prometey</td>
<td>60</td>
<td>0.5</td>
<td>15</td>
<td>Oxidation</td>
<td>Gap between spinel and magnetite</td>
<td>[Müller, 2004]</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>7200</td>
<td>1 $\times 10^{-6}$</td>
<td>Prometey</td>
<td>60</td>
<td>0.5</td>
<td>5</td>
<td>Oxidation</td>
<td>New oxide layer</td>
<td>[Müller, 2004]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>600</td>
<td>18</td>
<td>1500</td>
<td>$1 \times 10^{-6}$</td>
<td>IPPE</td>
<td>60</td>
<td>1.3</td>
<td>-200</td>
<td>Dissolution</td>
<td>[Müller, 2002]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>400</td>
<td>150</td>
<td>1000</td>
<td>$2 \times 10^{-7}$ H$_2$/H$_2$O</td>
<td>LECOR</td>
<td>60</td>
<td>2</td>
<td>-100</td>
<td>Dissolution</td>
<td>Erosion started</td>
<td>[Fazio, 2003]</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>50</td>
<td>1000</td>
<td>$3-5 \times 10^{-6}$</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>0</td>
<td>Weight gain(mg/mm$^2$): 0.00</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>1000</td>
<td>$3-5 \times 10^{-6}$</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>7</td>
<td>Weight loss (mg/mm$^2$): 0.001</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>460</td>
<td>300</td>
<td>2000</td>
<td>$3-5 \times 10^{-6}$</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>3</td>
<td>Weight loss (mg/mm$^2$): 0.002</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>2000</td>
<td>$3-5 \times 10^{-6}$</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>18</td>
<td>Weight gain(mg/mm$^2$): 0.019</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>460</td>
<td>300</td>
<td>3000</td>
<td>$3-5 \times 10^{-6}$</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>4</td>
<td>Weight gain (mg/mm$^2$): 0.00</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>550</td>
<td>300</td>
<td>3000</td>
<td>$3-5 \times 10^{-6}$</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>21</td>
<td>Weight gain(mg/mm$^2$): 0.00</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L tube</td>
<td>460</td>
<td>300</td>
<td>1000</td>
<td>$3-5 \times 10^{-6}$</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>0</td>
<td>Local corrosion No surface treat. Weight gain (mg/mm$^2$): 0.002</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L rod</td>
<td>550</td>
<td>1000</td>
<td>$3-5 \times 10^{-6}$</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>1</td>
<td>Local corrosion No surface treat. Weight gain (mg/mm$^2$): 0.01.</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L rod</td>
<td>460</td>
<td>2000</td>
<td>$3-5 \times 10^{-6}$</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>0</td>
<td>Local corrosion No surface treat. Weight loss (mg/mm$^2$): 0.002</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L rod</td>
<td>550</td>
<td>2000</td>
<td>$3-5 \times 10^{-6}$</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>2</td>
<td>Local corrosion No surface treat. Weight gain (mg/mm$^2$): 0.00.</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L rod</td>
<td>460</td>
<td>300</td>
<td>3000</td>
<td>$3-5 \times 10^{-6}$</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>0</td>
<td>Local corrosion No surface treat. Weight gain (mg/mm$^2$): 0.000</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>T (°C)</td>
<td>ΔT</td>
<td>Time (hours)</td>
<td>[O] (%wt.)</td>
<td>OCS</td>
<td>Loop</td>
<td>LBE volume (litres)</td>
<td>Flow rate (m/s)</td>
<td>Oxide thickness/dissolution depth (microns)</td>
<td>Remark 1</td>
<td>Remark 2</td>
<td>Ref.</td>
</tr>
<tr>
<td>--------------</td>
<td>--------</td>
<td>----</td>
<td>--------------</td>
<td>------------</td>
<td>--------------</td>
<td>------------</td>
<td>-------------------</td>
<td>----------------</td>
<td>---------------------------------------------</td>
<td>--------------------------------------------------</td>
<td>--------------------------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>316L rod</td>
<td>550</td>
<td>300</td>
<td>3000</td>
<td>3.5 × 10⁻⁶</td>
<td>CU-1M (IPPE)</td>
<td>60</td>
<td>1.9</td>
<td>2</td>
<td>Local corrosion No surface treat. Weight loss (mg/mm²): 0.02.</td>
<td>[Li, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS316</td>
<td>550</td>
<td>959</td>
<td>5 × 10⁻⁷</td>
<td>1M (IPPE)</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>2</td>
<td>30</td>
<td>Oxidation Porous layer. Weight loss (g/m²): 62.</td>
<td>[Takahashi, 2002]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS316</td>
<td>550</td>
<td>1000</td>
<td>3.6 × 10⁻⁷</td>
<td>1M (IPPE)</td>
<td>H₂/H₂O = 0.12-2.2</td>
<td>2</td>
<td>-100</td>
<td>Dissolution</td>
<td>[Takahashi, 2002]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>400</td>
<td>1500</td>
<td>1 × 10⁻⁹</td>
<td>LECOR</td>
<td>1</td>
<td>-0.64</td>
<td>Dissolution Weight loss (mg/mm²): 0.0225</td>
<td>[Aiello, 2004]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>400</td>
<td>4500</td>
<td>1 × 10⁻⁹</td>
<td>LECOR</td>
<td>1</td>
<td>-19.5</td>
<td>Dissolution Weight loss (mg/mm²): 0.155</td>
<td>[Aiello, 2004]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>400</td>
<td>1500</td>
<td>10⁻³-10⁻⁷</td>
<td>CHEOPE III</td>
<td>1</td>
<td>1</td>
<td>Oxidation Weight gain (mg/mm²): 2.9 × 10⁻³</td>
<td>[Aiello, 2004]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>400</td>
<td>3000</td>
<td>10⁻³-10⁻⁷</td>
<td>CHEOPE III</td>
<td>1</td>
<td></td>
<td>Oxidation Weight gain (mg/mm²): 3.91 × 10⁻³</td>
<td>[Aiello, 2004]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6.3.7. Steels in stagnant Pb

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Time (hours)</th>
<th>[O] (%wt.)</th>
<th>OCS</th>
<th>Surface sample/ LBE volume ratio</th>
<th>Oxide thickness/ dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Remark 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optifer IVc</td>
<td>550</td>
<td>800</td>
<td>$8 \times 10^{-6}$</td>
<td>H$_2$/H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Müller, 2000]</td>
</tr>
<tr>
<td>Optifer IVc</td>
<td>550</td>
<td>1500</td>
<td>$8 \times 10^{-6}$</td>
<td>H$_2$/H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Müller, 2000]</td>
</tr>
<tr>
<td>Optifer IVc</td>
<td>550</td>
<td>3000</td>
<td>$8 \times 10^{-6}$</td>
<td>H$_2$/H$_2$O</td>
<td></td>
<td>35 Oxidation</td>
<td></td>
<td></td>
<td>[Müller, 2000]</td>
</tr>
<tr>
<td>1.4970</td>
<td>550</td>
<td>800</td>
<td>$8 \times 10^{-6}$</td>
<td>H$_2$/H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Müller, 2000]</td>
</tr>
<tr>
<td>1.4970</td>
<td>550</td>
<td>1500</td>
<td>$8 \times 10^{-6}$</td>
<td>H$_2$/H$_2$O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Müller, 2000]</td>
</tr>
<tr>
<td>1.4970</td>
<td>550</td>
<td>3000</td>
<td>$8 \times 10^{-6}$</td>
<td>H$_2$/H$_2$O</td>
<td></td>
<td>16 Oxidation Pb inclusions at the oxide/ material interface</td>
<td></td>
<td></td>
<td>[Müller, 2000]</td>
</tr>
<tr>
<td>F82H</td>
<td>464</td>
<td>700</td>
<td>Argon</td>
<td></td>
<td>8 Oxidation</td>
<td></td>
<td></td>
<td></td>
<td>[Fazio, 2001]</td>
</tr>
<tr>
<td>F82H</td>
<td>464</td>
<td>1200</td>
<td>Argon</td>
<td></td>
<td>20 Oxidation</td>
<td></td>
<td></td>
<td></td>
<td>[Fazio, 2001]</td>
</tr>
<tr>
<td>316L</td>
<td>464</td>
<td>700</td>
<td>Argon</td>
<td></td>
<td>Oxidation Not measurable</td>
<td></td>
<td></td>
<td></td>
<td>[Fazio, 2001]</td>
</tr>
<tr>
<td>316L</td>
<td>464</td>
<td>1200</td>
<td>Argon</td>
<td></td>
<td>2-4 Oxidation</td>
<td></td>
<td></td>
<td></td>
<td>[Fazio, 2001]</td>
</tr>
<tr>
<td>F82H</td>
<td>520</td>
<td>2000</td>
<td>Argon (saturation)</td>
<td>13.7cm$^2$/0.3 l</td>
<td>20 Oxidation Weight gain: 0.0741</td>
<td></td>
<td></td>
<td></td>
<td>[Benamati, 2000]</td>
</tr>
<tr>
<td>F82H</td>
<td>520</td>
<td>3700</td>
<td>Argon (saturation)</td>
<td>13.7cm$^2$/0.3 l</td>
<td>40 Oxidation Weight gain: 0.1652</td>
<td></td>
<td></td>
<td></td>
<td>[Benamati, 2000]</td>
</tr>
</tbody>
</table>
Table 6.3.8. Steels in flowing Pb

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>ΔT</th>
<th>Time (hours)</th>
<th>[O] (%wt.)</th>
<th>OCS</th>
<th>Loop</th>
<th>LBE volume (l)</th>
<th>Flow rate (m/s)</th>
<th>Oxide thickness/dissolution depth (microns)</th>
<th>Remark 1</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optifer Ivc</td>
<td>400</td>
<td>1027</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>36</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optifer Ivc</td>
<td>550</td>
<td>1027</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>44</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optifer Ivc</td>
<td>400</td>
<td>200</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>44</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optifer Ivc</td>
<td>550</td>
<td>200</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>44</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optifer Ivc</td>
<td>400</td>
<td>3027</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>44</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>550</td>
<td>1027</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>36</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>550</td>
<td>3027</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>25</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4948</td>
<td>400</td>
<td>1027</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>2</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4948</td>
<td>550</td>
<td>1027</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>2</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4948</td>
<td>400</td>
<td>2000</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>2</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4948</td>
<td>550</td>
<td>2000</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>2</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4970</td>
<td>400</td>
<td>1027</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>2</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4970</td>
<td>550</td>
<td>1027</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>2</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4970</td>
<td>400</td>
<td>2000</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>2</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4970</td>
<td>550</td>
<td>2000</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>2</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4970</td>
<td>400</td>
<td>3027</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>2</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4970</td>
<td>550</td>
<td>3027</td>
<td>3.4 x 10^{-5}</td>
<td>IPPE</td>
<td>60</td>
<td>2</td>
<td>2</td>
<td>Oxidation</td>
<td>[Glasbrenner, 2001]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
REFERENCES


Long Bin (2003), IWMHR, Rome.


Chapter 7

EFFECT OF LBE AND LEAD ON MECHANICAL PROPERTIES OF STRUCTURAL MATERIALS*

7.1 Introduction

The use of heavy liquid metals, and especially of lead-bismuth eutectic (LBE) or lead for accelerator-driven systems (ADS) and lead-cooled (Pb) or lead-alloy-cooled (primarily Pb-Bi) fast reactor (FR) concepts of Generation IV requires an assessment of their compatibility with structural materials. Their deployment requires that the materials compatibility issue will be resolved, with and without irradiation, either under the mixed proton-neutron spectrum typical of the spallation source of an ADS in the one case, or under the fast neutron spectrum typical of an FR in the other case. The irradiation effects on structural materials in contact with HLM are the subject of a dedicated chapter.

One should not forget the experience gained with liquid metal-cooled FRs in industrialised countries. However, practically all these reactors have used sodium as their coolant, excepting the Russia. Moreover, the expertise on compatibility of stainless steels with sodium is not transferable to lead and lead alloys, due to the significant differences in their physics and metallurgic properties\(^1\) [Gorse, 2006].

Certainly, the older literature dedicated to the mechanical properties of steels, from carbon steels to high Cr steels, in contact with lead and lead alloys is essentially of Russian origin: the research on HLMs technology will soon cover one century, early oriented toward developing a fundamental understanding of the LME mechanisms since the Rebinder discovery [Rebinder, 1928], then largely R&D oriented at the beginning of the fifties with the development of submarine propulsion reactors in parallel with two full scale ground test reactor facilities, using LBE as a coolant [Gromov, 1997].

In a European country like France, that early opted for the sodium-cooled FR concept with Rapsodie, Phénix, then Superphénix, the R&D continued in parallel on other reactor concepts, like for example the molten salt reactor (MSR) concept between 1970 and 1983, using a cooling system operating by direct contact between the salt and the molten lead. In this context, a harmful effect of reducing lead\(^2\) on the tensile properties of Chromesco 3 and EM12 ferritic steels was noticed between 300 and 350°C [Broc, 1983], corroborating an earlier Japanese study [Tanaka, 1969]. The possible influence of lead on the fatigue strength of these steels remained unknown. In the US, a Pb-Bi cooled reactor was considered in the early fifties, and then abandoned in favour of sodium cooling [Manly, 1954]. In Japan, as in Europe and in the US, the sodium-cooled FR option was selected, with the related R&D for JOYO and MONJU. In Japan, as in many other countries, one finds also in the

\* Chapter lead: Dominique Gorse (CNRS, France). For additional contributors, please see the List of Contributors included at the end of this work. Thanks are expressed to J-B. Vogt (CNRS-LMPGM), T. Auger (CNRS-CECM) and V. Ghetta (CNRS-LPSC) for interesting and fruitful discussions.

\(^1\) Omitting voluntarily the difference in the nuclear (activation) and neutronic properties between Na and Pb or LBE, which is well outside the scope of the present chapter.

\(^2\) Lead made reducing by introduction of a deoxidising agent (Zr, Ti…) and bubbling of an Ar-5%H\(_2\) mixture, since the OCS technology developed in USSR was not yet redeveloped in Europe.
literature some studies dedicated to specific solid/liquid model systems [Mae, 1991] to the aim of improving the understanding of liquid metal embrittlement (LME), or to the aim of solving some industrial problems. The Japanese literature on mechanical resistance of materials in contact with LMs is thus varied, going from basic papers aimed at understanding LME [Ina, 2004] to patents related to materials resistant to LME [Kanetani, 1992], to the evaluation of the resistance to embrittlement of metals in the environment [Funaki, 1993].

It is a fact that, in R&D devoted to nuclear systems using corrosive lead or LBE as a coolant, compatibility is generally associated to little or controlled corrosiveness [Loewen, 2003]. Lead or LBE induced corrosion is unacceptable to insure long-term safe operation of a future reactor.

In this context, the present chapter presents a review of the published works on the effect of LBE or lead on the mechanical behaviour of the 316L austenitic stainless steel and the T91 martensitic steel pre-selected for the design of a future European transmutation facility (EFIT, XT-ADS), in the framework of the EUROTRANS programme of FP6.

To provide as complete information as possible on ferritic/martensitic steels in contact with lead or lead alloys, the results of some studies carried out as part of the fusion programmes, on related steel grades like MANET, OPTIFER, 1.4914 in contact with Pb-17Li or even lithium, and also in contact with LBE are also included when available. Since information on 316L in contact with lead or LBE is lacking in some areas, the results of some studies conducted either as part of liquid metal fast breeder reactor (LMFBR) programmes on type 316 steel in contact with sodium, or as part of the spallation neutron source projects on type 316 steel in contact with mercury, and if possible on 316 type steel in contact with lead or LBE, are also included when available.

In this chapter, the tensile behaviour, then the fatigue and creep-fatigue behaviour, and finally some creep properties are presented and discussed. The fracture properties are just mentioned but not discussed, in absence of available data. The focus will be on T91 steels and 316L stainless steels in contact with LBE or lead. This chapter is organised as follows:

- Section 7.2 focuses on liquid metal embrittlement (LME). It is subdivided into two parts. Section 7.2.1 is dedicated to wetting, which is one of the two main requirements for occurrence of LME, and today the only one for which there is some data available on real systems, in addition to an abundant theoretical literature. Section 7.2.2 is devoted to the definition of LME, the criteria of occurrence of this phenomenon and presents the simplest analysis of the LME failure.
- Section 7.3 is dedicated to a closely related phenomenon, environment-assisted cracking (EAC), which permits an interpretation of the results of some tensile tests conducted on T91 or 316L steel in lead or LBE environment.
- The effect of lead or LBE on the tensile properties of T91 is well documented, thanks to the European TECLA and MEGAPIE-TEST programmes of FP5. The results are summarised in Section 7.4. The tensile behaviour of 316 type stainless steel in contact with LBE or lead is less documented.

3 For steel makers, LME studies are conducted to improve the machinability of steels, to understand the crack failure of hot-dip galvanised steel structures, or to develop weldability of metallic alloys.
4 EFIT: European Facility for Industrial Transmutation; XT-ADS: eXperimental demonstration of the technical feasibility of Transmutation in an Accelerator Driven sub-critical System.
6 TECLA: Technology, Thermohydraulics for Lead Alloys, European programme granted by the EU 5th Framework Programme.
Today, and in spite of a lack of quantitative results on fatigue and fracture, based on an analysis of the data collected on the tensile behaviour, shown in Tables 7.4.1 to 7.4.8 and on the fatigue behaviour, shown in Tables 7.5.1 and 7.5.2, the question of the susceptibility to LME of T91 in contact with LBE and how to proceed from the metallurgical and chemical points of view to promote or hinder LME effects can be addressed. This is the subject of Sections 7.4.3 and 7.4.4.

The effect of LBE and lead on the fatigue behaviour of T91 steel is reported in Section 7.5. As concerns 316L, limited results in LBE are shown. Studies of fatigue crack growth for both T91 and MANET II in LBE are summarised in Section 7.5.5.

The effect of lead or LBE on the creep properties of both T91 and 316L are extremely limited. Data published from the fusion or LMFBR programmes represent the total data set available. A short paragraph, Section 7.6.4, will be dedicated to the phenomenon of liquid metal accelerated creep (LMAC), which includes the results of four-point bending tests carried out on T91 in contact with lead around 525°C in Section 7.6.5.

Information on fracture mechanics, from fracture toughness to crack growth behaviour in contact with LBE does not exist: in Section 7.7 are summarised the actions defined by the EU partners of the EUROTRANS programme for future work.

Section 7.8 is dedicated to recommendations for testing procedures.

A short conclusion terminates this chapter.

### 7.2 Liquid metal embrittlement

Liquid metal embrittlement (LME) is a physico-chemical and mechanical process, the interpretation of which is largely based on the wetting concept. For this reason a discussion of the wetting process is presented first in Section 7.2.1. Section 7.2.2 deals with the definition of LME, the criteria for occurrence of LME and presents a widely accepted explanation of the brittle LME failure.

#### 7.2.1 Wetting: From ideal to real metallic systems

The study of the wetting, i.e. of the spreading of a liquid on a solid was first reported at the beginning of the 19th century with Laplace and Young [Young, 1805]. From the theoretical point of view, a renewal of interest was initiated by de Gennes in the early 80s [Leger, 1992], [de Gennes, 2002]. From the practical point of view, there are a number of applications, such as paints, lubrication, gluing, cosmetology, without forgetting metallurgical processes like hot dip coating [Ebrill, 2000].

While the theoretical understanding improved since Young, it is worth emphasising that real solid/liquid (S/L) metal systems still remain too complex to allow for predictions of the spreading of one oxidisable metal alloy onto another metal alloy of different electronic and physicochemical properties, exhibiting thus differing oxidation properties (see Chapters 2, 3 and 4). Consequently, in most cases, experimental work is required in conditions that mimic the real situation of interest.

In the following, we shall consider first ideal S/L systems, second non-interacting metal-metal systems, then interacting S/L systems, including ceramic-metal systems. Finally we conclude with a discussion of the wettability of steels by HLMs.

---

7 Such a paints, lubrication, gluing, cosmetology, without forgetting metallurgical processes like hot dip coating [Ebrill, 2000].
Ideal solid/liquid systems

Ideally, for a homogeneous and smooth surface, only partially wetted by a “simple” liquid, a liquid drop, small enough to neglect the gravity effects, does not spread and retains a spherical shape characterised by the contact angle between the liquid-vapour interface and the solid-liquid interface at the contact line where these two interfaces merge. The equilibrium contact angle $\theta_E$ is determined by the values of the surface tensions between the three phases. Each of these surface tensions is a force per unit length of the contact line, tangential to the interface, tending to retract the interface. At mechanical equilibrium, the horizontal components of these forces balance (Figure 7.2.1, left). This is the Young law:

$$\cos \theta_E = (\gamma_{lv} - \gamma_{sl})/\gamma_{lv}$$

(7.1)

with $\gamma_{sv}$, $\gamma_{sl}$, $\gamma_{lv}$ being respectively the solid-gas, solid-liquid and liquid-gas surface tensions. Eq. (7.1) can be rewritten in terms of the spreading coefficient $S = \gamma_{lv} - (\gamma_{sl} + \gamma_{lv})$, as:

$$S = \gamma_{lv} (\cos \theta_E - 1)$$

(7.2)

showing that $\theta_E$ can be defined only in case of partial wetting with $S < 0$.

**Figure 7.2.1.** *Left:* The mechanical equilibrium of the solid-liquid-vapour triple line determines the value of $\theta_E$. *Right:* Liquid metal drop spreading completely on a solid substrate ($S > 0$) or not ($S < 0$) until attainment of the equilibrium contact angle $\theta_E$.

Total wetting is characterised by $S > 0$ with the drop spontaneously spreading and tending to cover the solid surface (Figure 7.2.1, right).

In less ideal situations, taking into account the heterogeneities, the chemical contamination and the roughness of the solid surface, one does not measure the equilibrium contact angle $\theta_E$ of the Young law, but at best a steady state contact angle depending on the history of the system. If the liquid-vapour interface has been obtained by advancing the liquid (after spreading of a drop), the contact angle has a value $\theta_A$ larger than the equilibrium value $\theta_E$. The advancing contact angle $\theta_A$ is defined as the threshold value beyond which the contact line begins to move when the liquid advances (Figure 7.2.2). If, on the contrary, the liquid-vapour interface has been obtained by receding the liquid (by aspiration or retraction of the drop), the measured contact angle $\theta_R$ is smaller than the equilibrium contact angle $\theta_E$. $\theta_R$ is defined as the limit value without moving the contact line by aspiration of the drop (Figure 7.2.2). Intuitively, the advancing contact angle $\theta_A$ is larger than the equilibrium contact angle $\theta_E$, which is again larger than the receding contact angle $\theta_R$: $\theta_R < \theta_E < \theta_A$. 

278
The difference \( \theta_A - \theta_R (>0) \) informs on how far from ideal is the surface state. The hysteresis \( |\theta_A - \theta_R| \) can reach tens of degrees depending on the surface conditions, whether it is contamination or roughness. The prediction of the wetting hysteresis of a randomly rough real surface will always be difficult due to the lack of determination of the relevant size of defects on/in the surface. Note that one knows today that the triple line can stick at very small defects of micrometric size [de Jonghe, 1995]. This suggests that if one wants to classify the wettability of real surfaces by a given liquid, the experimental procedure must be extremely rigorous [de Gennes, 2002].

Non-interacting metal-metal systems

This condition is idealised by ignoring the potential influence of impurities and especially oxygen at the interface, after de Gennes [de Gennes, 2002]. The spreading coefficient \( S \) is determined by the respective Van der Waals interactions in both phases in contact and at the interface. \( S \) can thus be re-written as:

\[
S = V_{sl} - V_{ll}
\]  

(7.3)

with \( V_{sl} \) and \( V_{ll} \) being respectively the Van der Waals energy at the S/L interface and in the liquid phase. Wetting will be generally good and even total if the liquid is less polarisable than the solid. Note that Eq. (7.3) describes a situation where there is no electronic and ionic charge transfer at the S/L interface. At the macroscopic scale, this means no mass transfer between two immiscible phases (no oxidation, no corrosion reactions).

For interacting S/L systems (e.g. ceramic-metal)

In this case, so-called reactive wetting occurs by successive stages accompanied by interfacial reactions, changing de facto the nature of the interface. Dynamic non-equilibrium wetting occurs with the spreading rate of the initially non-interacting system, determination of a first quasi-equilibrium contact angle, followed by a modification of the spreading rate due to interfacial reactions, until attainment of an equilibrium contact angle at the interface between new phases of a priori different composition, structure and properties [Nakae, 1992]. In case of reactive wetting, the contact angle obeys the empirical law:

\[
\cos \theta_{\text{min}} = \cos \theta - \frac{\Delta \gamma_r}{\gamma_{lv}} - \frac{\Delta G_r}{\gamma_{lv}}
\]

(7.4)

with \( \Delta \gamma_r \) and \( \Delta G_r \) being respectively the change of interfacial energy brought about by the interfacial reaction(s) and the change in free energy per unit area released by the reaction of the material contained in the immediate vicinity of the metal substrate interface [Espié, 1994]. It has been proposed that spreading occurs because \( \Delta G_r \) is at least partially transformed to interfacial energy [Naidich, 1981]. Note that until now there is no generally accepted theory capable of describing reactive wetting satisfactorily. As noted above, experimental work is necessary for each interacting S/L system of interest. However, as far as ceramic-metal model systems are concerned, equilibrium phase diagrams are available and help perhaps not to predict the wetting behaviour but at least to explain the observed wetting behaviour.
Interacting steel/HLM systems

For interacting steel/HLM systems, like T91-LBE and T91-lead, or 316L-LBE and 316L-lead couples, the following points are immediately noticeable:

1) It is very difficult to predict the wettability of a Cr-containing steel (like T91, 316L…) by molten HLMs (Pb, Pb-55Bi, Pb-17Li, Hg…) and to verify *a posteriori* that a wetting angle, if measurable [Chatain, 1993], is acceptable, since research on the equilibrium phase diagrams for such multi-component systems is very new. The reader should read the studies on the Bi-Fe-Hg-O-Pb quinary systems or on the Bi2O3-Fe2O3 pseudo-binary system performed by A. Maitre, J-C. Gachon and co-workers during the last five years [Maitre, 2002, 2004, 2005]. To be more precise, today, it is impossible to predict whether lead and/or bismuth will form stable phases with one of the components of the T91 steel substrate (essentially Fe and/or Cr), if and how reactive wetting will occur. However, XPS analysis of the oxidised T91-lead interface has revealed the presence of lead at the steel/oxide interface [Gamaoun, 2003].

2) Being unpredictable, the wettability of steels (T91, 316L) by lead, LBE and other liquid metals must be determined in each experimental situation, as function of the composition and structure of the interfacial oxide film [Medina, 2006]. It is once again worth emphasising that a meaningful steady state contact angle will not be obtained if the surface state and overall experimental procedure are not rigorously controlled, according to the recommendations of Section 7.8.8.

3) It is generally observed that an oxidised metal or metal alloy is at most partially wetted ($\theta_e < 90^\circ$) or poorly wetted ($90^\circ \leq \theta_e \leq 130^\circ$) by a liquid metal. The tendency to spreading can be estimated if one knows the value of the liquid-vapour surface tension of the LM of interest in contact with the steel surface. Several measured values for the surface tension of liquid metals are listed in Table 7.2.1.

   For example, considering T91 steel or, more specifically, some Russian steels grades with a significant Si content (from 0.4 to 1.3 wt.%), a plausible hypothesis is that for some temperatures and oxygen activities, the uppermost surface layers of the oxidised steel will be essentially a silicon oxide. Considering that the surface tension of SiO2 should be of the order of 150 mN/m, no wetting of the steel by Bi, Pb or Hg is expected based on the high values of surface tensions reported in Table 7.2.1.

4) As of this date, there are few reliable studies concerning the wetting of lead or LBE on T91 steel. On a diamond-polished T91 steel specimen, a contact angle of $126 \pm 5^\circ$ was found at 380°C with 99.9999% pure lead by using a sessile drop setup installed in a ultra high vacuum (UHV) chamber [Lesueur, 2002]. This contact angle did not change whatever the annealing time and volume of the lead drop. This result is consistent with the presence of a FeCr2O4 oxide film onto the T91 steel surface. These results have been corroborated by other works performed on the T91-lead system at 450°C by V. Ghetta, *et al.* [Ghetta, 2001] (see Figure 7.2.3).

As shown above, the oxidised T91 steel is poorly wetted by lead in the 380-450°C range. Certainly, wetting studies of T91 and 316L steel in either “reducing” or “oxidising” lead and LBE, covering the 450-600°C temperature range would be of interest in the future.

Long-term aging in flowing and even stagnant HLM may modify the surface state, with successive phases of stability/instability of the surface oxide. Correlatively a non-wetting → wetting “transition” could occur, with consequences on the potential damages due to the HLMs.

---

8 See, for example, the influence of microscopic defects on the pinning of the triple line [Leger, 1992].
Table 7.2.1. Surface tension of some liquid metals at the melting point or just above in vacuum or under rare gas (He, Ar…), with exception of Pb-55%Bi for which the temperature of the measurement is indicated. The surface tension is given in mN/m (= dyne/cm).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Surface Tension (mN/m)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td>118</td>
<td>[Passerone, 1998]</td>
</tr>
<tr>
<td>Sodium</td>
<td>191 ≤ γ_{Na} ≤ 205</td>
<td>[Handbook, 1966]</td>
</tr>
<tr>
<td>Bismuth</td>
<td>376 ≤ γ_{Bi} ≤ 390</td>
<td>[Handbook, 1966]</td>
</tr>
<tr>
<td>Bismuth</td>
<td>370 ≤ γ_{Bi} ≤ 410</td>
<td>[Novakovic, 2002]</td>
</tr>
<tr>
<td>Bismuth</td>
<td>389</td>
<td>[Passerone, 1998]</td>
</tr>
<tr>
<td>Lithium</td>
<td>399</td>
<td>[Passerone, 1998]</td>
</tr>
<tr>
<td>Lead</td>
<td>450 ≤ γ_{Pb} ≤ 480</td>
<td>[Handbook, 1966]</td>
</tr>
<tr>
<td>Lead</td>
<td>471</td>
<td>[Passerone, 1998]</td>
</tr>
<tr>
<td>Lead</td>
<td>443 ≤ γ_{Pb} ≤ 480</td>
<td>[Novakovic, 2002]</td>
</tr>
<tr>
<td>Lead-55%Bismuth</td>
<td>406 at 350°C</td>
<td>[Novakovic, 2002]</td>
</tr>
<tr>
<td>Lead-55%Bismuth</td>
<td>391 at 500°C</td>
<td>[Pokrovskii, 1969]</td>
</tr>
<tr>
<td>Mercury</td>
<td>435 ≤ γ_{Hg} ≤ 485</td>
<td>[Handbook, 1966]</td>
</tr>
<tr>
<td>Mercury</td>
<td>498</td>
<td>[Passerone, 1998]</td>
</tr>
<tr>
<td>Magnesium</td>
<td>577</td>
<td>[Passerone, 1998]</td>
</tr>
</tbody>
</table>

Figure 7.2.3. Lead drops on T91 steel after 15 days exposure to a reducing stagnant lead bath under OCS at 450°C; note that the contact angles $\theta_{c}$ are larger than 90°, and approach 130°

7.2.2 Definition and criteria of occurrence of LME

Slight differences between the definitions of LME can be found in the literature. The reader should return to the review papers on LME by Rostoker [Rostoker, 1960], Westwood [Westwood, 1963], Kamdar [Kamdar, 1973], Nicholas [Nicholas, 1979], Gordon [Gordon, 1982], to the recent models review by B. Joseph [Joseph, 1999], to the point of view of E.E. Glickman in 2000 [Glickman, 2000]. The very important former USSR literature was stimulated by Academician P.A. Rebinder, since its discovery in 1928 [Rebinder, 1928]. A new field of research, referred to as “physico-chemical mechanics”, headed by Rebinder, started in 1954 and lasted until the end of the twentieth century… [Likhtman, 1954, 1958, 1962], [Shchukin, 1977, 1999].

The following definition is proposed: LME is the reduction in ductility and strength that can occur when normally ductile metals or metallic alloys are stressed whilst in contact with liquid wetting metals.
LME is considered as a special case of brittle fracture, intergranular (IG) or transgranular (TG) by cleavage, that occurs in absence of an inert environment and at low temperature.\(^9\) Last, LME is accompanied by little or no penetration of the embrittling atomic species into the solid metal [Kamdar, 1973]. In other words, strictly speaking, a time and temperature dependent fracture process will not be considered as a manifestation of LME.

In this line, corrosion or diffusion-controlled grain boundary penetration of a solid metal by a liquid metal, that occurs under tensile stress tending to zero or even stress independent,\(^10\) which characterise a limited number of well-known metallic couples like Al-Ga or Zn-Hg… is considered as a liquid metal induced damage, irrelevant in the present chapter.

LME failure occurs by nucleation of a crack at the wetted surface of a solid and its subsequent propagation into the bulk until ultimate failure. Work is still strongly needed to clarify this very old and tricky problem in physical metallurgy. Single crystals can be susceptible to LME [Likhtman, 1962]. In this case, a model including all physico-chemical and metallurgical aspects, from initiation to intermittent crack growth [Goryunov, 1978] until final rupture, is still strongly missing. This is also the case of real materials, in spite of the potentially pre-existing crack embryos. Today, for real materials prone to LME, the main issue is why and how some micrometric or nanometric cracks will remain stable whereas others (at least one), made unstable, will develop under the influence of the embrittling metal atoms filling the crack until the crack tip [Clegg, 2001], [Ina, 2004]. In some cases, crack propagation is also found spasmodic in polycrystals.\(^11\) A crucial issue is why and how the presence of embrittling metal atoms accelerates the crack kinetics [Glickman, 2000]. Note that the embrittling metal phase, often considered as a macroscopic liquid controlling the crack propagation [Robertson, 1966] is also sometimes considered as a “quasi-liquid” with approaching the crack tip area [Rabkin, 2000]. In short, this means that, in the future, a multi-scale modelling approach will be necessary to account for all LME failures. This is not the scope of this chapter. However, this had to be underlined in this Chapter of which one target will be to examine the susceptibility to LME of some new systems with respect to the today available literature reviews [Nicholas, 1979, 1981, 1982]…

The prerequisites for LME are listed below:

1) Intimate or direct contact at the atomic scale between the solid and liquid metal phases, a concept classically interpreted as wetting.

2) Applied stress sufficient to produce plastic deformation, even if the required deformation may be produced, on a microscopic scale, at stresses much below the engineering yield point.

3) The existence of stress concentrators or pre-existing obstacles to the dislocations motion. This requirement is a matter of controversy, and is not considered as important as the two already mentioned criteria.

In the discussion, we shall come back to the concept of wetting, in general considered macroscopically and thermodynamically. It will appear that the behaviour of structural materials in contact with liquid metals can be rationalised only if one discriminates properly non reactive from reactive wetting. Most often, assumptions will be made to produce consistency between the various literature sources.

---

\(^9\) We do not consider here high-temperature liquid metal embrittlement.

\(^10\) And the related macroscopic phenomenon of grain separation and decohesion.

\(^11\) For example, spasmodic crack propagation was observed with a Russian ferritic/martensitic steel in contact with lead [Abramov, 1994]. See Table 7.4.10 in the annex to this chapter.
A widely accepted explanation of the LME failure is based on the Griffith criterion establishing the fracture stress $\sigma_F$ for crack propagation [Griffith, 1920], modified to take into account the Rebinder effect, i.e. the reduction of the surface free energy, $\gamma_{sl}$, by adsorption of a liquid metal with respect to an inert environment [Rebinder, 1928]. $\sigma_F$ is written as follows:

$$\sigma_F = \frac{E\gamma_{sl}}{2c}$$  \hspace{1cm} (7.5)

where $E$ is the Young modulus, and $c$ is the crack dimension or its radius in case of an internal flaw as shown in Figure 7.2.4. [Griffith, 1920]. Eq. (7.5) supposes that the change in stored elastic strain energy is entirely used in the fracture process to create fresh fracture surfaces.

**Figure 7.2.4.** Flat crack, of length $2c$ and width $2r$, in a sheet, subject to a tensile stress $\sigma$, perpendicular to the crack length

In *real* situations, rupture does not proceed as a result of the development of an elastic microcrack since a crack cannot be stable in an ideal lattice; as soon as it appears, it will develop at a rate of the order of the sound velocity throughout the whole crystal, if there is no barrier to its development. Assuming that a stable crack serves as a stress concentrator, this crack already exists in the deformed lattice. Thus plastic deformation first occurs, and only after a stable crack may appear and survive at the so-called subcritical stage, so long as the stress intensity factor $K$, written $K=Y\sigma\sqrt{\pi c}$ with $Y$ being a geometric correction factor and $c$ the crack length, does not attain the threshold $K_{C,LME}$.

In *real* situations, Rebinder and Shchukin [Rebinder, 1972] proposed to include the plastic deformation of the material accompanying crack growth, and to write a critical fracture stress as:

$$\sigma_c = \mu (E/c)^{1/2} \left(\gamma_p + \gamma_{sl}\right)^{1/2}$$  \hspace{1cm} (7.6)

where $\mu$, $E$, $\gamma_p$ and $\gamma_{sl}$ are respectively a proportionality coefficient, the Young modulus, a contribution to the plastic deformation and the solid-liquid interfacial free energy defined above. This expression is still the central point of all Russian models of LME. The correctness of Eq. (7.6) was already questioned by Popovich [Popovich, 1979]. At this point it is worth recalling that, until now, in the literature, there is no analytical expression of the fracture stress, accounting for the energy to create a new fresh surface wetted by a liquid metal and the plastic energy to form the plastic zone around the crack tip.

The consequences of metal adsorption on softening or strengthening of the surface layers is still a matter of discussion in metallurgy in the absence of a universal modelling of dislocation-atomic impurities interactions and consequences on plastic flow.
At this point, it is worth mentioning that the necessary condition of “intimate contact at the atomic scale between the solid and liquid metal phases” for occurrence of LME, which can be reformulated as the metal adsorption condition due to Rebinder, implicates various physico-chemical macroscopic processes that include: 1) dissolution and formation of dealloyed layers possibly brittle (as in SCC modelling) in the case of corrosive LM; 2) inter-atomic mixing and formation of surface alloys whose consequences depend on the SM/LM system in case of limited solubility between the two metallic phases, a concept that may be interpreted diversely; 3) no exchange, at the atomic scale, between the two solid and liquid phases, considered immiscible, which is rigorously impossible to prove experimentally.

7.3 Environment-assisted cracking

7.3.1 Definition of EAC

Environmentally-assisted cracking refers to the premature and catastrophic failure of a material in the simultaneous presence of a tensile stress and an even possibly only mildly corrosive environment.

7.3.2 Phenomenological criteria of occurrence of EAC

The prerequisites for EAC are the following:

1) Liquid-metal-induced corrosion (LMC), that may be localised, intergranular or uniform, or to the contrary that may lead to the growth of an oxide film at the solid metal surface, is considered as a main requirement for occurrence of EAC. As indicated above, the corrosiveness of the LM may be very limited, affecting only the superficial solid layers.

2) Plastic deformation, interacting with corrosion, characterises EAC at all stages of the process.

It is worth recalling that corrosion and consequently EAC are time-dependent. Therefore a liquid metal induced degradation of the mechanical properties that will be indubitably function of the ageing time in the LM will be considered as a case of EAC in the following discussion of the data in Section 7.4. Let us note that the crack velocity in EAC never attains the values reported in LME, which may attain $10^{-1}$ m/s for some embrittling couples [Glickman, 2000].

Nevertheless, so long as LME and EAC are not better understood, which is the situation today, so long as the wetting concept intervening in LME is defined macroscopically, and in case there is some doubt about the fracture surface, corroded or not, wetted or not, it may happen that the fracture of a material in contact with a liquid metal will be considered as a manifestation of LME or EAC depending on the author.

In order to discriminate properly between these two related phenomena, EAC and LME, it is essential to properly characterise the surface state in contact with the LM phase, at the appropriate scale. Once passed this crucial phase, the metallurgical and mechanical parameters for either LME or EAC failure could be better defined [Glickman, 2000], [Gorse, 2000].
7.4  Tensile behaviour of austenitic and ferritic/martensitic steels in contact with lead, LBE and other liquid metals

7.4.1  Definitions

The tensile test consists of the application of an increasing load on a specimen, which will progressively deform and fracture it. Typically the data are presented as load as a function of specimen elongation. Tensile tests are usually displacement controlled, but they can be also load controlled. The uniaxial tension specimen with a circular cylindrical gage-length represents an extremely useful and convenient test-geometry for studying the constitutive behaviour of materials. An ongoing application of tensile tests is the study of fracture processes in metals. They are used in Sections 7.4.2, 7.4.3, 7.4.4 and 7.4.5 to assess the susceptibility to LME and EAC of the T91-LBE or T91-lead couples.

From the recording of the engineering stress-strain curve (load divided by the initial section area versus elongation normalised by the initial length \( L_0 \)), the following data can be obtained: 1) yield strength \( (R_{p0.2}) \) at a specific value of the engineering stress for a given value of the plastic strain, conventionally 0.2%; 2) ultimate tensile strength (UTS) \( (R_m \) or \( \sigma_{UTS} \)), the maximum value of engineering stress during the test \( (F_m/S_0) \); 3) the effective yield strength \( (\sigma_{eff}) \), average of the 0.2% yield and the ultimate tensile strength; 4) the total elongation \( (A\%) \), \( 100 \times (L_f - L_0)/L_0 \) elongation of the specimen at fracture, where \( L_f \) is the length of the gage length after fracture and the total elongation is the sum of the uniform elongation and of the post necking elongation; 5) the reduction of area \( (Z\%) = 100 \times (S_0 - S_u)/S_0 \) where \( S_u \) is the section area after fracture (usually elliptical, due to anisotropy).

7.4.2  Tensile behaviour of smooth, rough and notched martensitic steel specimens in HLMs

The experimental results are collected in Tables 7.4.1 to 7.4.8 in the annex to this chapter. The chemical compositions of the studied steels are reported in Table 7.4.9 below and in the annex to this chapter.

7.4.2.1  Tensile behaviour of smooth and rough T91 steel specimens in lead, LBE and tin

The first tests were conducted on electro-polished specimens at 350°C in oxygen-saturated lead, and resulted in a ductile fracture of T91 [Legris, 2000, 2002], [Verleene, 2006]. No change was found after 1 hour of tempering at 500°C. Combining the effect of a notch and of a hardening thermal treatment was apparently required to obtain a brittle failure, not only in Pb at 350°C, but also in LBE and Sn at 260°C [Nicaise, 2001], [Legris, 2002]. A ductility trough was estimated in between 350 and 425°C for T91 in oxygen-saturated lead [Vogt, 2002].

In Table 7.4.2, the tensile data for notched T91 in contact with stagnant LBE are presented. The specimens are in the standard metallurgical state: normalised at 1050°C (1 h), then air cooled, followed by tempering at 750°C (1 h) and final air cooling. A preliminary study had revealed that it was possible to make LBE locally adherent onto T91 after 12 hours at 600°C or 650°C in an environment consisting of flowing He-4%H2 [Pastol, 2002]. In same environment (LBE under flowing hydrogenated helium) but at much lower temperatures of 200, 300°C, it was also shown that a thin oxide layer has grown after 12 h of exposure and that the as-formed oxide is easily spalling off without roughening the steel surface, to which LBE could possibly adhere. For these conditions, a deleterious effect of LBE has been shown [Pastol, 2002], [Guérin, 2003].

285
In Table 7.4.3, the tensile data of smooth specimens, diamond polished [Pastol, 2002] or electro-polished so as to remove the flaws unintentionally produced during the specimens preparation [Dai, 2006] are shown. For these conditions, oxygen-saturated LBE under vacuum, the steel specimens are rather well protected by an oxide film, certainly more efficiently after electropolishing than after diamond polishing and there is no effect on the tensile properties. Indeed, any LBE effect would be unlikely, due to the fact that the liquid metal cannot make contact with the oxidised steel surface, except in case where the oxide film would be intrinsically brittle, which is unexpected in this case.

Table 7.4.3 also presents the results of tensile tests performed on rough (unpolished) specimens, with the surface state resulting from coarse mechanical grinding [Sapundjiev, 2006]. No significant effect of LBE is found, in spite of the fact that the chemistry of the LM phase was carefully controlled. The absence of LBE-induced damage is consistent with the fact that the LM cannot wet the T91 steel with this surface condition.

7.4.2.2 Tensile behaviour of T91 steel specimens in LBE, in the presence of flaws

Table 7.4.4 is devoted to the deleterious effect of flaws on the tensile behaviour. These defects were unintentionally produced during the preparation of the tensile specimens [Dai, 2006b], [Glasbrenner, 2003]. Considering the set of data collected in [Dai, 2006b], for tests conducted between 250 and 425°C, a temperature effect was also evident. Such an effect can be rationalised if one considers that the penetration of the LM in the cracks is competing with the oxidation of the crack walls and the crack tip.

7.4.2.3 Tensile behaviour of MANET II and T91 steels after pre-exposure to LBE

In Table 7.4.5, the influence of pre-exposure to LBE for short or long durations (up to thousands of hours) in forced circulation (LiSoR, LECOR) loops, in either oxidising [Glasbrenner, 2003] or reducing [Fazio, 2003], [Aiello, 2004] conditions is reported. A loss of ductility was found for MANET II at 250 and 300°C in oxidising LBE [Glasbrenner, 2003], and for T91 at 400°C after exposure to reducing LBE [Aiello, 2004]. To the contrary, only a slight detrimental effect of 4000 h ageing in stagnant LBE was found on T91 at 450°C after tensile testing in LBE under hydrogenated argon [Sapundjiev, 2006]. This result is certainly due to the preparation procedure of the tensile specimens, coarse mechanical grinding not allowing for wetting by LBE, which explains the absence of embrittling effect (see Section 7.2.1). Traces of zinc in the LBE probably caused the brittle fracture of T91 steel at 380°C [Gamaoun, 2002, 2003] after at least one month preliminary ageing in pure LBE under the oxygen control system (OCS) adapted by V. Ghetta, et al. [Ghetta, 2001, 2002].

7.4.2.4 Tensile behaviour of T91 in air, at room temperature after pre-exposure to LBE

The results of Table 7.4.6 show that, whatever the surface state, with oxide formed during exposure at 650°C, with Pb-Bi locally adherent onto the steel surface (at T ≥ 600°C) or not (T < 300°C), the ductility of T91 steel is unaffected so long as the tensile tests are conducted at room temperature. The current conclusion is thus that solidified LBE is not embrittling, for the experimental conditions for which data exists. The effect of HLMs, liquid at or near room temperature, like mercury on the tensile behaviour of T91, was very recently investigated, and revealed that both the T91-Hg and 316L-Hg couples are embrittling [Medina, 2006].
7.4.2.5  Tensile behaviour of T91 in conditions of direct contact with Pb-Bi

Table 7.4.7 is devoted to the effect of Pb-Bi on the tensile behaviour of T91 in conditions of direct contact with the steel surface, in absence of interfacial oxide. Surface physics techniques were used to deoxidise the gage length of the cylindrical diamond-polished tensile specimens, and to deposit Pb-Bi layers [Auger, 2004, 2005]. These results clearly revealed a susceptibility of T91 to embrittlement by Pb-Bi.

7.4.2.6  Tensile behaviour and embrittlement of martensitic steels in contact with Li and Pb-17Li

The results of selected studies are reported in Table 7.4.8. Li causes (intergranular) corrosive attack of 1.4914 steel grade and a net degradation of the tensile properties for tests conducted in lithium, with and without preliminary exposure to Li [Borgstedt, 1986]. To the contrary, it is noticeable that pre-exposure to Pb-17Li in very different experimental conditions did not affect the mechanical properties (here tensile) of HT9, F82H-mod, OPTIFER IVb… In some cases, a pre-wetting treatment is mentioned, but a complete description of the surface state before and after the tensile test is often missing whereas, on the contrary, the chemistry of the melt is clearly described.

The study conducted on EUROFER 97 in the LIFUS loop is worth mentioning [Benamati, 2002]: the analysis of the surface state reveals that Pb-17Li is in direct contact with the steel surface as a result of long term ageing in the LIFUS loop. However, the tensile tests conducted on Pb-17Li wetted EUROFER 97 specimens under argon did not revealed any change in the tensile behaviour.

Table 7.4.9. Chemical compositions of the above mentioned steels (wt.%, balance Fe)

<table>
<thead>
<tr>
<th>Steel</th>
<th>Cr</th>
<th>W</th>
<th>Ni</th>
<th>Mn</th>
<th>V</th>
<th>Nb</th>
<th>Mo</th>
<th>Ta</th>
<th>Ti</th>
<th>Al</th>
<th>Cu</th>
<th>C</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>B</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromesco 3</td>
<td>2.09</td>
<td>–</td>
<td>–</td>
<td>0.50</td>
<td>–</td>
<td>–</td>
<td>1.09</td>
<td></td>
<td></td>
<td></td>
<td>0.085</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>EM 12</td>
<td>9.65</td>
<td>–</td>
<td>–</td>
<td>1.03</td>
<td>0.32</td>
<td>0.46</td>
<td>2.04</td>
<td></td>
<td></td>
<td></td>
<td>0.105</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>8.26</td>
<td>0.13</td>
<td>0.38</td>
<td>0.2</td>
<td>0.08</td>
<td>0.95</td>
<td>0.024</td>
<td>0.08</td>
<td>0.105</td>
<td>0.055</td>
<td>0.009</td>
<td>0.003</td>
<td>0.43</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MANET</td>
<td>10.37</td>
<td>0.657</td>
<td>0.76</td>
<td>0.21</td>
<td>0.16</td>
<td>0.5B</td>
<td>0.007</td>
<td>0.01</td>
<td>0.10</td>
<td>0.032</td>
<td>0.004</td>
<td>0.008</td>
<td>0.0075</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4914</td>
<td>10.6</td>
<td>0.82</td>
<td>0.54</td>
<td>0.24</td>
<td>0.19</td>
<td>0.49</td>
<td>0.05</td>
<td>0.04</td>
<td>0.172</td>
<td>0.005</td>
<td>0.005</td>
<td>0.002</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT9</td>
<td>11.8</td>
<td>0.52</td>
<td>0.51</td>
<td>0.30</td>
<td>0.31</td>
<td>1.03</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.21</td>
<td>0.21</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>F82H-mod</td>
<td>7.66</td>
<td>2.0</td>
<td>0.16</td>
<td>0.16</td>
<td>0.02</td>
<td>–</td>
<td>–</td>
<td>0.09</td>
<td>0.005</td>
<td>0.01</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OPTIFER IVb</td>
<td>8.3</td>
<td>1.4</td>
<td>0.34</td>
<td>0.22</td>
<td>–</td>
<td>–</td>
<td>0.06</td>
<td>–</td>
<td>0.12</td>
<td>0.03</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EUROFER 97</td>
<td>8.8</td>
<td>1.15</td>
<td>–</td>
<td>0.44</td>
<td>0.2</td>
<td>0.002</td>
<td>0.003</td>
<td>–</td>
<td>–</td>
<td>0.10</td>
<td>–</td>
<td>–</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[*] = [Legris, 2000, 2002], [Nicaise, 2001], [Vogt, 2002], [Pastol, 2002], [Gamaoun, 2002, 2003], [Guérin, 2003], [Auger, 2004, 2005], [Verleene, 2006], since the T91 steel whose composition is reported above was supplied by Creusot Loire Industrie in the frame work of the French GEDEON programme on structural materials for ADS.

7.4.3  Experimental results that may be interpreted as LME effects: Case of T91 in contact with LBE or lead

When the French, European (TECLA, MEGAPIE-TEST…) and international (MEGAPIE…) programmes on ADS began, there was little information about the compatibility of 9-12%Cr containing steels with lead and lead-bismuth alloys. The publications in Russian journals dedicated to the compatibility of structural materials with liquid lead or lead alloys were largely unknown, un-translated or poorly translated. This is for example the case of all studies dealing with the liquid metal induced failure of steels before 1955, which was the subject of a monograph of Ya.M. Potak [Potak, 1955b]. It would have been also interesting to know the works related to the mechanical properties of austenitic and ferritic/martensitic steels in contact with lead which were proposed for the
main components of the BREST-OD-300 reactor, and especially that liquid lead has practically no effect on the tensile properties of austenitic steels between 420 and 550°C or that the lead effect on the tensile properties of the selected 9Cr ferritic/martensitic steels simply consists in a decrease of elongation near the melting point at 350°C, and disappears at higher temperatures [Abramov, 2003]. It would have been also interesting to know that researches to optimise the composition and structure of steels for Pb-cooled, Pb-Bi-cooled reactors were done in Russia [Gorynin, 2000], [Solonin, 2001]. In this line, all information on the influence of HLMs on the mechanical properties of steels obtained to design and build the Russian reactor facilities by a very active scientific community was fully missing at the beginning of the EU, US and Asia programmes on ADS and LMFBRs.

Last, it would have been of primary importance to know that V.V. Popovich already noted in 1978 that wetting of iron and iron base alloys by lead or bismuth is not so easily achieved [Popovich, 1978], even when using the efficient method of the soldering fluxes and, consequently, that Pb or Bi should not be strong embrittlers of steels.

Thus, initially, T91 was pre-selected as a structural material for the European ADS project and for the MEGAPIE spallation target, due to its excellent mechanical properties under irradiation by fast neutrons. As mentioned above, it was a challenge to prove that contact with molten lead or LBE could produce LME effects. Now, after more than four years, it is known that T91 can be embrittled by LBE and it is possible to make a review, at least partial, of the metallurgical conditions producing LME effects. It is also possible to propose solutions to protect T91 steel against LME.

Let us keep in mind that, until now, the answer to the question of the susceptibility to LME of both the T91-LBE and T91-lead couples is only qualitative: it is based on an analysis of tensile tests reported in Tables 7.4.1 to 7.4.8 (see annex). A rigorously quantitative answer requires fatigue and fracture mechanics tests conducted in strictly controlled environmental conditions, such as the ones planned in the framework of the DEMETRA programme of FP6.12

In the following, we consider successively the role of the different parameters, which demonstrate a LME effect.

7.4.3.1 Role of the bulk metallurgical state

Application of a hardening heat treatment to smooth cylindrical specimens of T91 steel was not sufficient to produce an embrittling effect in contact with stagnant lead under air at 350°C, after J.B. Vogt and co-workers [Legris, 2000], [Nicaise, 2001]. The presence of a stress concentrator, like a notch machined in the hardened T91 steel smooth specimen, leads to brittle fracture in contact with not only liquid lead [Legris, 2000], [Nicaise, 2001] and LBE [Legris, 2002], but also with tin [Legris, 2002], over the temperature range from 260 to 350°C. The corresponding experimental load-elongation curves and fractography are reproduced in Figure 7.4.1.

Tensile tests on hardened notched T91 specimens, prepared as above, were also conducted in Hg (under air) and in air for comparison at 20°C [Legris, 2002]. Since a brittle fracture was found in both cases, with and without mercury, these results must be considered cautiously.

---

12 DEMETRA: DEvelopment and assessment of structural materials and heavy liquid METal technologies for TRAnsmutation systems, is one of five technical domains of the EUROTRANS programme granted by PF6.
Figure 7.4.1. a) Tensile test results of notched specimens obtained at 260°C in liquid Sn (full squares), in LBE (full circles), in air (open triangles) and at 350°C in liquid lead (full diamonds) and in air (open squares); b) SEM micrograph of the fracture surface obtained in LBE at 260°C.

For the T91-Pb couple, a ductility trough was found to extend from about 350 to 425°C. It is noticeable that the tests were all conducted in oxygen-saturated lead, with fully oxidised specimen surfaces, unwetted. This suggests that crack initiation required, at the same time, oxide film breakdown accompanying some localised plasticity. Otherwise, the fracture would intervene at identical stress level, independently of the liquid metal phase, which is not the case.

To conclude this paragraph, so long as the mechanical tests are carried out on oxidised T91, in oxygen-saturated HLM (Pb, Pb-55Bi, Sn, Hg), the combination of a hardening heat treatment and of a notch machined in the tensile T91 specimens is required to produce LME effects.

These results were later confirmed by H. Glasbrenner and F. Gröschel [Glasbrenner, 2004] on U-bent T91 specimens, hardened by means of the hardening heat treatment applied above by J-B. Vogt and co-workers (one hour tempering at 500°C, air cooling). Deep cracks, filled with LM, were found on the bent regions of the specimens exposed for 1000 hours to bismuth or Pb-17Li at 300°C. No such effect was found after 1000 hours exposure to LBE at 300°C, these results suggesting the existence of a stable and protective superficial oxide film. No oxygen control system (OCS) was in place in the system at 300°C. Improvements of the OCS allowing for reliable measurements at temperatures in the range of 350°C and below are recent [Ghetta, 2001, 2002], [Courouau, 2002, 2004]. The fact that Pb-Bi is less corrosive than bismuth and less reducing than Pb-Li does not justify the obtained results, which cannot be interpreted today. The authors suggest that the harmful effect of LBE could be just delayed. However, as recalled above in the definition of LME, a fracture process that is a function of the environmental conditions and more precisely time and temperature dependent cannot be, strictly speaking, considered as a pure manifestation of LME.

7.4.3.2 Role of wetting

T91 steel is highly oxidisable and passivatable, due to its 9% chromium content. As a result, its native oxide film is stabilised after a few hours of ageing in the laboratory environment. It has been shown that the native oxide film on T91 does not dissolve in high purity (99.9999%) lead at 380°C after prolonged ageing [Lesueur, 2002]. At the same time, it has also been shown that T91 is poorly wetted by lead over the 380-450°C range, even in presence of active OCS in the melt.
Indirect contact via an oxide film

First, the hypothesis was made that short ageing in LBE, which is more corrosive than pure lead, would allow for removing gently and at least partially the thin oxide film grown after 12 hours in LBE, avoiding surface roughening and permitting some (localised) wetting of T91 by LBE:

- As long as un-notched specimens were tested, no effect of LBE was detected over the 200-450°C temperature range, neither under vacuum, nor under hydrogenated helium.
- When notched specimens were tensile tested, after standard heat treatment and careful surface preparation (cf. Section 7.8), a damaging effect of LBE was found, strongly dependent on the liquid and gas phases in contact as is shown in Figure 7.4.2. The reduction in strength and ductility, undetectable at 200°C, passes through a maximum at 350°C before beginning ductility recovery at 400°C. The effect of LBE, maximised under He-4%H₂, was shown in ductility and energy to rupture, with a clear dependence on the deformation rate against oxidation rate [Guérin, 2003].

Figure 7.4.2. Load versus cross-head displacement curves obtained with notched T91 specimens, after standard heat treatment, at 350°C for a cross-head displacement rate of 6.7 × 10⁻⁴ mm/s, showing the environmental effects: vacuum (V), LBE under vacuum (V+LBE), He-4%H₂, LBE under He-4%H₂ (He-4%H₂ + LBE)

However, in the above experiment [Guérin, 2003], the surface state was not rigorously controlled, smooth at submicroscopic scale and wetted, by comparison with the experiment that will be described now [Auger, 2004].

In order to remove the oxide film so as to wet the T91 steel and check whether the T91-LBE couple is embrittling, there are different methods of surface preparation. We focus on the more efficient ones.

Direct contact via physical vapour deposition

To deoxidise the T91 steel, without roughening, corroding and contaminating the steel surface, it is necessary to proceed under UHV. The oxide film is removed by argon ion sputtering in an UHV chamber, followed by physical vapour deposition of Pb-Bi layers of thickness of order of a few hundred of nanometers. After tensile testing at 340°C under helium at a strain rate of 10⁻⁴ s⁻¹, brittle
fracture is observed with a number of small cracks on the gauge length of the T91 specimen as shown in Figure 7.4.3, after T. Auger, et al. [Auger, 2004 and 2005]. The fracture process is controlled by the reservoir of embrittling atoms at the specimen surface.

**Figure 7.4.3.** *Top:* In case of direct T91-LBE contact obtained by ion beam sputtering in an UHV chamber prior to deposition of Pb-Bi by PVD, LME effects are produced at 340°C under He. *Bottom left:* SEM micrograph (SE2) of the multi-cracked gauge length of the T91 specimen. *Right:* SEM micrograph (SE2) of an initiation site close to the surface showing a quasi cleavage fracture surface.

Intimate contact by means of chemical fluxes

This method was largely employed in the former USSR In almost all reported works [Abramov, 1994], [Antipenkov, 1991], [Balandin, 1970], [Bichuya, 1969], [Chaevskii, 1962, 1969], [Dmukhovs’ka, 1993], [Gorynin, 1999], [Nikolin, 1968], [Popovich, 1978, 1979, 1983], [Soldatchenkova, 1972], the intimate contact between Armco iron or other Russian steel grades and a potentially embrittling metal (Cd, Ga, Bi, Pb, Sn... or their alloys) is forced by using the method of the soldering fluxes.
De facto, the hypothesis is made that the flux does not perturb the experiment with residual impurities at the steel/LM interface. This drawback, inherent to the method, was minimised by the Russian scientists. For pre-tinning steels specimens with LBE, the employed soldering flux contains zinc, known as a strong embrittler. Balandin tested the mechanical properties of steel specimens in liquid Pb-Bi containing 0.05 to 0.1% Zn and found results comparable to those obtained with pre-tinned specimens tested in pure Pb-Bi [Balandin, 1970]. This does not constitute a proof that Zn does not affect the results of the mechanical tests.

Wetting of T91 steel by LBE has also been achieved by the method of the soldering fluxes. However, the LME effects obtained under these conditions are not reproduced here, because of the embrittling influence of the chemical impurities, and especially zinc, at the steel-LBE interface. In fact, brittle failure of T91 in stagnant LBE containing traces of zinc was observed by F. Gamaoun [Gamaoun, 2003]. To give another example in a different context, a harmful effect of zinc as an impurity in flowing sodium on the creep life of a type 304 SS at 550°C was noted by Huthmann [Huthmann, 1980].

Once again, it appears that the surface preparation is a crucial phase to determine the susceptibility to LME of a given solid-liquid couple.

Last, let us note that dewetting of Armco iron (0.37%C), initially coated with Pb, Bi or LBE by the method of soldering fluxes, may occur due to interfacial oxidation caused by atmospheric oxygen inward diffusion, throughout the embrittling metal layers [Popovich, 1978]. At this point, it could be mentioned that the inward diffusion of oxygen toward the interface could affect the results of the mechanical tests before that dewetting becomes macroscopically observable. However, the remarkable efficiency of the method of the soldering fluxes was proved by Yu.F. Balandin in a study of a 12 KhM pearlitic steel in contact with LBE: the author has shown that, after exposure to oxygen saturated LBE for durations going from 2.5 hours to 25 hours at 500°C, re-tinning with LBE restores its embrittling effect [Balandin, 1970].

7.4.3.3 Role of surface flaws

At the microscopic scale, cracks formed over the whole surface of the tensile specimen invariably promote premature brittle fracture of T91 steel when in contact with LBE. This was shown by different authors, in different environmental conditions [Vogt, 2002], [Dai, 2006], [Fazio, 2003].

Specimen preparation by EDM cutting, even followed by mechanical polishing, results in micro-cracks, randomly distributed over the whole specimen surface, which act as incipient cracks susceptible to propagate rapidly in contact with LMs, and produce LME effects. Moreover, the stress-strain state due to EDM cutting is also unknown. The detrimental effect of EDM-cutting was observed recently by Y. Dai, on flat tensile specimens over a wide temperature range extending from 300 to 425°C, in oxygen saturated LBE under argon, as illustrated in Figure 7.4.4 at 325 and 375°C [Dai, 2006]. Some scattering in the results (particularly the elongation to rupture) is unavoidable with an uncontrolled distribution of micro-cracks, filled or not by LBE, which is absolutely unpredictable. Moreover, the advance of the cracks filled with LBE is always competing with the oxide film formation on crack walls and at crack tip, which is also unpredictable.

The potentially embrittling effect of sharp micro-cracks generated in the cold worked area that forms in the notch during its mechanical machining has been observed [Vogt, 2002]. During loading of hardened and notched T91 steel specimens, the micro-cracks in the notched zone will propagate under the influence of the liquid metal.
Figure 7.4.4. Top: Microcracks due to EDM-cutting. Before (left) and after (right) tensile testing in LBE; note that all pre-cracks are not filled by LBE. Bottom: Tensile test results of mechanically polished EDM-cut specimens obtained. At 325°C in oxygen-saturated LBE under argon (left) and at 375°C in oxygen-saturated LBE under argon (right).

The exposure time to LBE prior testing is indicated. The propagation of the micro-cracks filled by LBE is revealed during tensile testing.

Figure 7.4.5. a) Comparison of stress-strain curves obtained in argon and in oxygen-saturated LBE (no OCS) in LiSoR loop at 250 and 300°C. b) SEM micrograph showing the mixed fracture surface obtained with MANET II after tensile testing at 300°C in LBE.
Under the LiSoR loop conditions, a mixed fracture surface was obtained with both flat and ductile areas. The final surface preparation of the tensile specimen was not specified. However, the presence of small cracks initially present onto the specimen surface, propagating under the influence of liquid Pb-Bi, and more specifically bismuth as indicated by the Authors, is a plausible hypothesis, possibly more plausible than the suggestion that the specimens of MANET II could be wetted by LBE under these conditions at 250 or 300°C after two hours pre-exposure to oxidising LBE before tensile testing. Note that ductile failure was always obtained for MANET II in LBE at the lower temperatures tested of 180 and 200°C.

7.4.3.4 Role of traces of impurities

An example of the embrittling effect of zinc, even at trace levels, was shown by F. Gamaoun during his PhD thesis [Gamaoun, 2003]. Cylindrical smooth specimens of T91, diamond polished, were first exposed for one month at 525°C in reducing LBE. The specimens were then submitted to a relaxation test in LBE at 380°C for a few days, and finally ruptured by tensile testing at the same temperature. The main characteristics of the test results were: 1) a significant reduction of the elongation to rupture; 2) a brittle fracture; 3) a surface completely covered with LBE, adherent over the whole gauge length.

A reasonable assumption is that the so obtained surface state and the brittle failure obtained during tensile testing were promoted by traces of zinc in the liquid LBE, as already mentioned above.

The embrittling effect of zinc, antimony and tin, alloyed to lead, was emphasised by W.R. Warke, K.L. Johnson and N.N. Breyer in a review paper of 1970 [Warke, 1970]. However these authors were considering their role as alloying elements, and not at the level of trace elements…as is the case here. Note that the influence of trace elements on mechanical properties in metallurgy remains today a matter of debate.

7.4.4 Main requirements to prevent LME effects

The following conditions must be fulfilled to prevent LME effects:

1) Excellent surface finish of the steel surface, which must be free of surface defects such as pre-cracks, scratches as a result of the surface preparation, and also free of inclusions or precipitates which could act as stress concentrators and initiate cracks in service conditions.

2) The presence of a protective oxide film on to the steel surface prior and during contact with the liquid metal, and self-healing in service conditions. This can be achieved by implementation of an OCS in the system. However, no OCS is required in the case of oxygen-saturated HLM during the entire life of the installation of interest [Bichuya, 1969].

3) No specific recommendation on the oxide film thickness, provided that the film remains adherent to the steel surface, with sufficient plasticity. This supposes an adapted oxide film composition and structure, which must be determined and controlled over the test duration, in each experimental situation of interest [Bichuya, 1969].

4) The temperature must be chosen outside the ductility trough, above the upper temperature limit, which means, for example:
   - T ≥ 425°C for T91, after hardening heat treatment and using notched specimens in oxygen-saturated lead [Nicaisce, 2001], [Vogt, 2002];
   - T ≥ 400°C for T91, after standard heat treatment, and using notched specimens in oxygen-saturated LBE [Guérin, 2003].
There is no rigorous proof that the range of the lower temperature limit, close to the melting point or below the melting point of the embrittling metal, must be avoided. However, besides LME, solid-metal-induced embrittlement (SMIE) is a well-known phenomenon. Some manifestations of SMIE are famous in the literature [Gordon, 1982], which strongly suggests that one keeps the system above the upper limit of the ductility trough. This supposes a systematic study of the influence of the temperature and strain rate to determine the ductility trough of each new steel-HLM system, if no reliable data are available. This supposes also that the metallurgical state of the steel and the chemistry of the HLM be controlled over the entire testing procedure.

5) Control of the presence of impurities: attention must be paid to metallic embrittling impurities like zinc, antimony, tin, and to metalloid impurities and also to chloride and fluoride species not only in the liquid metal phase but also at all stages of the specimen preparation, especially if one uses the method of the soldering fluxes to wet the steel under study. Their presence, even as trace elements, may affect significantly the mechanical properties [Huthmann, 1980].

7.4.5 Experimental results that may be interpreted as EAC effects

We comment briefly on the tensile tests performed on pre-corroded 1.4514 steel grade, HT9, F82H-mod, OPTIFER IVb and EUROFER 97 in contact with Li or Pb-17Li, all reported in Table 7.4.8. Then we come back to the tensile properties of pre-corroded T91 in contact with LBE collected in Table 7.4.5 (see Annex).

7.4.5.1 Case of some ferritic/martensitic steels in contact with Li and Pb-17Li

H.U. Borgstedt, et al. [Borgstedt, 1986] observed that corrosive attack, superficial and at pre-cracks, induced by prolonged pre-exposure of 1.4914 steel to pure stagnant lithium at 500°C does not influence the stress-strain curves obtained during tensile tests conducted in air. To justify these results, it was reasonably argued that only the surface but not the bulk properties are affected during aging in contact with lithium. However, when the specimens pre-exposed to lithium were tensile tested in lithium at 250°C, the fracture behaviour changed, exhibiting both brittle and ductile fracture areas, but the specimens always retained some amount of plastic strain at rupture.

O.K. Chopra and D.L. Smith [Chopra, 1986] did not observe any influence of flowing Pb-17Li at temperatures between 273 and 454°C on the tensile behaviour of normalised and tempered HT9, that was preliminary exposed to flowing Pb-17Li at 427°C for 18 hours in order to wet the HT9 specimens by Pb-17Li.

T. Sample and H. Kolbe [Sample, 2000] confirmed those findings in a study of two low activation steels – F82H-mod and OPTIFER IVb – in the fully tempered martensitic state. After a pre-wetting treatment of 15 hours at 500°C in Pb-17Li under argon, the tensile properties were found unchanged in Pb-17Li at 250 and 400°C. After 1500 to 4500 hours exposure to Pb-17Li at 480°C in the LIFUS II loop, G. Benamati, et al. did not observe any degradation of the tensile properties of EUROFER 97 during testing under argon at 480°C, whereas the specimen surface was largely corroded by Pb-17Li, and poorly adherent corrosion layers were present on the steel surface [Benamati, 2002].

It is worth remembering that lithium and Pb-17Li are both reported to be reducing and corrosive media. Exposure to Li or Pb-17Li at high temperature (from 427°C [Chopra, 1986] to 480 [Benamati, 2002] and 500°C [Sample, 2000]) invariably corrodes and roughens the steel surface, less for the ferritic/martensitic steel here considered than for an austenitic steel, but this is not the point.
Consequently, assuming that complete wetting can be achieved by pre-heating at high temperature from tens to hundreds of hours depending on the authors, this is not the wetting between two metals with negligible mutual solubility, in other words the wetting required for occurrence of LME, after Kamdar. Therefore, the consequences of such reactive wetting on the mechanical properties remain today totally unpredictable. They will depend on the corrosion processes occurring prior to or under mechanical loading. In all cases, we consider that the degradation of the mechanical properties of martensitic steels caused by contact with Pb-17Li is a manifestation of EAC.

7.4.5.2 Case of T91 steel in contact with LBE

In the framework of the TECLA and MEGAPIE-TEST programmes, G. Benamati, C. Fazio, et al. studied the T91-LBE couple using the above described experimental procedure (see Table 7.4.5): long-term exposure of T91 to flowing and reducing Pb-55Bi at 400°C in the LECOR loop (1500-4500 h) followed by tensile test under argon at same temperature [Fazio, 2003], [Aiello, 2004].

The oxygen level in the melt, ranging from $3 \times 10^{-10}$ to $10^{-7}$ wt.ppm was lowered by addition of Mg and bubbling under pure H$_2$. The results are: i) a net reduction of the elongation to rupture, ii) a decrease of the ultimate tensile strength, iii) with mixed ductile (at the centre) and brittle (at the periphery) fracture surfaces (Figure 7.4.6).

These results tend to demonstrate that the surface state obtained after such long-term ageing in Pb-55Bi is the one required to produce embrittlement. Today, with all that we know about EAC and LME phenomena, these results could be interpreted as a manifestation of either EAC or LME.

Very recently, a detrimental effect of long-term exposure to LBE on the tensile properties of T91 was also observed by D. Sapundjiev, et al. [Sapundjiev, 2006]. This work also shows an effect of the ageing temperature, clear at 450°C but undetectable at 300°C (Figure 7.4.7). The results of this study are not in so good agreement with the ones described from the beginning of this chapter. This could be explained by the conditions of specimen preparation (mechanical grinding not followed by any surface treatment to minimise the roughness of the tensile specimens) and testing procedure, differing from the ones applied in the other quoted works.

In all cases, a systematic analysis of the composition and structure of the interface with the liquid is lacking, and also of the transport properties of metal ions elements throughout the interface. A better knowledge of the composition, structure and transport at the S/L interface would permit interpretation without ambiguity the obtained results.

7.5 Fatigue behaviour of austenitic steel of type 316 and ferritic/martensitic steel of type T91 in contact with lead and LBE

7.5.1 Definition

Among the different definitions for the term “fatigue”, the most appropriate for the materials of concern in this chapter is as follows: Fatigue is the progressive, localised and permanent change that occurs in a material subjected to conditions that produce fluctuating stress and strain at some points and that may culminate in cracks or complete fracture after a certain number of fluctuations.
Figure 7.4.6. a) Stress-strain curves obtained at 400°C in argon at strain rate of 3.10^{-3} \text{s}^{-1} after long term exposure of T91 to LBE at 400°C in LECOR loop. b) Morphology of T91 specimens after 4500 h in LECOR loop at 400°C followed by tensile testing in argon at 400°C. c) SEM micrograph showing a zone at the periphery of the fracture surface of the T91 tensile specimen [Aiello, 2004].

Figure 7.4.7. Engineering stress-strain curves obtained with T91 specimens, after standard heat treatment, after 4000 h pre-exposure to LBE at 450°C, followed by tensile test at 300 and 450°C at a strain rate of 5.10^{-5} \text{s}^{-1}. 

![Diagram of stress-strain curves](image)
The procedures of “fatigue testing” can be classified into four groups:

- the stress life approach;
- the strain life approach;
- the fatigue crack propagation approach;
- the component test model approach.

Corrosion-fatigue is one of the environmentally-assisted cracking phenomena.

The strain life and fatigue crack propagation approaches have been investigated in the framework of the French GEDEPEON programme, TECLA and MEGAPIE-TEST European programmes on ADS by J-B. Vogt, *et al.* [Vogt, 2004, 2006], [Verleene, 2006]. This was motivated by the fact that information on the resistance to crack initiation, the behaviour of small cracks and the crack velocity under cyclic loading in contact with LBE were extremely sparse. Consequently, low-cycle fatigue (LCF) as well as fatigue crack propagation (FCP) tests in HLMS were developed:

- FCP tests inform about the velocity of long cracks. Pre-cracked specimens, of CT or four-point bend type, are used. The test is generally performed under load control and requires the measurement of the single crack advance that propagates through out the specimen. The results are compiled into a relationship of type $da/dN = f(\Delta K)$ where $da/dN$ is the crack velocity expressed in mm/cycle and $\Delta K$ the stress intensity factor range.

- LCF tests inform about the cyclic accommodation of a material and characterise the resistance to crack initiation under cyclic loading. It uses smooth specimens (cylindrical, or hourglass shape gage length, plates). LCF tests are conducted under total or plastic strain control, with $\Delta \varepsilon$, ranging from 0.4% to 2.5%, generally with a triangular waveform and constant strain rate (in the range of $10^{-2}$ to $10^{-4}$ s$^{-1}$). Stress-strain hysteresis loops are periodically recorded during cycling allowing for the measurement of the stress range $\Delta \sigma$. The LCF life is equal to the number of cycles required to initiate surface cracks, and the propagation of at least one of them to failure.

Fatigue testing began on T91 in contact with LBE in the framework of the MEGAPIE target project. There were at least two motivations. Design of the target window has to ensure that cyclic loading imposed to the target window by the beam trips is less than the critical load leading to crack initiation after about $10^4$ load cycles, i.e. the expected lifetime foreseen for the LBE liquid metal target. Besides the beam trips, the structural materials of an ADS, especially the target container, will be subjected to a variety of loading conditions in service, thermo-mechanical or not.

When the French GEDEPEON and European programmes on ADS started, the information was extremely sparse about the effect of both lead and LBE on the fatigue behaviour of ferritic/martensitic steels like T91, MANET II... This is no longer the case [Kalkhof, 2003], [Vogt, 2004, 2006], [Verleene, 2006].

In some aspects, the situation is different as concerns the fatigue behaviour of 316 type austenitic stainless steels:

- In the framework of the fusion programme, the compatibility of 316L type SS with lithium or Pb-17Li, its corrosion and mechanical behaviour including low-cycle fatigue (LCF) have been extensively studied for decades [Borgstedt, 1991], [Chopra, 1983], [Benamati, 1994].
• In the framework of the LMFBR project, the fatigue behaviour of 316L type SS in contact with alkali metals, particularly sodium and lithium, was also thoroughly investigated for years now [Borgstedt, 1991], [Mishra, 1997], [Kalkhof, 2003].

• Recently, in the framework of the Japanese or US projects of spallation neutron sources, the compatibility of type 316LN stainless steel with mercury has been the subject of a number of works, since a type 316LN SS was selected for the vessel containing mercury [Strizak, 2001, 2003], [Tian, 2003].

However, to our knowledge, besides the former USSR literature concerning carbon steels and various Russian steel grades pre-tinned with LBE, tin or tin-lead eutectic [Bichuya, 1969], [Nikolin, 1968], [Chaevskii, 1969], [Popovich, 1979], [Dmukhovs'ka, 1995]…the effects of lead or LBE on the fatigue behaviour of 316 type SS are largely unknown. In the following, we briefly comment recent results [Kalkhof, 2003], [Vogt, 2004, 2006], [Verleene, 2006].

7.5.2 Low-cycle fatigue behaviour of ferritic/martensitic steels in contact with LBE

We first recall the conditions of the study due to D. Kalkhof and M. Grosse [Kalkhof, 2003]: Fully reversed (R = -1) strain controlled LCF tests were performed on a Schenck servo-hydraulic machine with a load capacity of 250 kN, at total strain amplitude (\(\varepsilon_{am}\)) varying from 0.2% to 1% (i.e. total strain range \(\Delta \varepsilon\) varying from 0.4% to 2%) at 1 Hz cycle frequency, with some tests conducted at \(\Delta \varepsilon = 0.3\%\) and 0.1 Hz frequency. The environmental conditions are air or stagnant LBE at 260°C, with no indication of the oxidising or reducing power of LBE. Some tests were also carried out in air at room temperature.

The conditions of the study of J-B. Vogt, I. Serre, et al. are based on the ASTM standard E 606 (Annual book of ASTM standards – 1991, Section 3, Vol. 03.01) [Vogt, 2004, 2006], [Verleene, 2006]: LCF tests were carried out at 300°C in air and in oxygen-saturated LBE under air, using a hydraulic MTS closed loop servo-controlled machine with a load capacity of 100 kN. A cylindrical vessel containing the HLM surrounded the specimen. Tests were total axial strain controlled using a strain gage extensometer set outside the HLM vessel. They were conducted in a fully push pull mode (R = -1) at different imposed total strain ranges: 0.4\% \leq \Delta \varepsilon \leq 2.5\%, using a triangular waveform and a control of the strain rate (\(4.10^{-3}\) s\(^{-1}\)). Hence, the cyclic frequency ranged from 0.25 Hz to 0.08 Hz for the smallest and highest strain tests respectively. During cycling, hysteresis loops were periodically recorded allowing for the measurement of the stress variation \(\Delta \sigma\) at each cycle. The fatigue life is defined as the number of cycles for which a 25% drop in the quasi stabilised tensile stress occurs.

In all cases, attention was paid to the surface state of the specimens, carefully manually polished [Kalkhof, 2003], or electro-polished [Vogt, 2004, 2006] depending on the authors.

The LCF behaviour of MANET II and T91 in contact with LBE or lead at \(\Delta \varepsilon < 0.3\%\) is unknown.

7.5.2.1 Role of LBE on cyclic accommodation

Cyclic softening was observed for both MANET II [Kalkhof, 2003] and T91 [Vogt, 2004], independent of the environment, air or stagnant LBE, in the previously described experimental conditions. This point is illustrated for the T91-LBE couple in Figure 7.5.1. These results suggest that LBE affects only the surface but not the bulk properties.
7.5.2.2 Role of LBE on fatigue resistance

For 316L [Kalkhof, 2003], the fatigue lives in LBE appeared to be similar when compared to the results in air especially at low strain amplitude where scatter in the fatigue lives was observed. At higher strain amplitudes ($\varepsilon_{\text{m}} = 0.5, 0.6\%$), there was a little influence of LBE on the fatigue resistance as is shown in Figure 7.5.2.

This contrasts very much with the behaviour of both MANET II [Kalkhof, 2003] and T91 [Vogt, 2004], [Verleene, 2006] whose fatigue life is reduced in contact with LBE as shown in Figure 7.5.2. The effect is function of the total strain amplitude and cycle frequency. The main trend is a decrease of fatigue life, amplified with increasing $\Delta \varepsilon_i$ and decreasing cycle frequency.

Figure 7.5.2. Total strain amplitude vs. cycle number for crack initiation curves for 316L stainless steel in air and PbBi at 260°C, after Kalkhof and Grosse
The oxygen activity in the LBE was not mentioned by Kalkhof. This information would have been of interest, since the surface state of the steel, either MANET II, T91 or 316L SS, is already largely modified by oxidation/corrosion at 260°C.

**7.5.3 Influence of hold time on fatigue behaviour of T91 in LBE**

Data as a function of hold time are presented in Figure 7.5.3 (Table 7.5.2 in annex and [Vogt, 2006]). The tests were performed under strain control, using a trapezoidal wave-form, with 10 min. tension hold time. The environmental conditions were 300°C in air or oxygen-saturated LBE.

**Figure 7.5.3. Fatigue resistance of T91 in air and in LBE, with and without 10 min hold time in tension. As an example, for Δε_t = 0.7%, the fatigue life is reduced of a factor ~2 at 300°C in oxygen-saturated LBE and by a factor of ~4 if a hold time is introduced.**

![Fatigue resistance of T91 in air and in LBE, with and without 10 min hold time in tension.](image)

The stress response to strain cycling is unmodified by the introduction of a hold time, either in air or in LBE. No stress relaxation was recorded at this temperature. On the contrary, for all tests performed at imposed total strain ranges in between 0.4% and 2.5%, the fatigue life of T91 decreases with application of a hold time in tension, contributing to the modification of the surface state in contact with LBE at 300°C. A synergistic effect of the environment and the mechanical test conditions may explain this decrease of LCF life. No such effect was observed in air.

**7.5.4 Influence of preliminary exposure to LBE on fatigue behaviour of T91**

A first batch of specimens was exposed in a LBE loop for 613 h at 600°C in reducing conditions (oxygen content less than $10^{-10}$ wt.%). Another batch was exposed to oxygen-saturated LBE (air over-pressure of 200 mbar) at 470°C for 502 hours. They were then fatigued in LBE at 300°C with the mechanical testing conditions reported in Table 7.5.2: strain control, symmetrical triangular wave form (R = -1) [Vogt, 2006]. The stress responses to strain cycling of T91 steel in LBE at 300°C after pre-exposure to LBE in either oxidising or reducing conditions, under OCS, were similar to that of non-exposed specimens.
The results of LCF tests are shown in Figure 7.5.4. The following results were observed:

- Cyclic softening was unaffected by preliminary ageing in LBE, whatever the conditions.
- Fatigue life was significantly decreased by preliminary ageing in reducing LBE.
- Fatigue life was unmodified or slightly increased by preliminary ageing in oxidising LBE.

**Figure 7.5.4.** Influence of pre-exposure of T91 to LBE under reducing or oxidising conditions (under OCS, in collaboration with A. Terlain, CEA-Saclay) on the fatigue resistance at 300°C in LBE under air. Note that the fatigue life of T91 aged in oxidising LBE is similar to that of the reference in air (AIR—as received), but larger than the fatigue life of T91 aged in reducing LBE for $\Delta e_i \sim 0.4\%$, the effect being less marked for $\Delta e_i \sim 0.9\%$.

### 7.5.5 Influence of LBE on fatigue crack growth of T91 and MANET II

Strictly speaking, only fatigue crack growth rate tests using pre-cracked specimens can give quantitative information on the effect of LBE.

However, a qualitative behaviour or tendency can be obtained from LCF tests. Indeed, the final decrease of the stress amplitude (see Figure 7.5.1) is related to crack propagation in the bulk. It was found that the stress decrease was more abrupt in LBE than in air suggesting that the crack growth rate is accelerated by LBE for both 316L [Kalkhof, 2003] and T91 [Kalkhof, 2003], [Verleene, 2006].

Crack propagation is faster in LBE than in air for MANET II and T91, in roughly similar testing conditions (see Table 7.5.1).

This result will be corroborated by making use of a more quantitative approach [Verleene, 2006], based on a specific experimental procedure of the AFNOR standard A03.404 (1991). Tests were carried out using four-point bend specimens (10 mm × 10 mm × 55 mm) under load control. The crack opening displacement (COD) was measured using a strain gage extensometer. The COD was converted into crack length using a calibration procedure, which allowed the calculation of both the crack growth rate $da/dN$ (mm/cycle) and the cyclic stress intensity factor $\Delta K$ (MPa.$\sqrt{m}$). Pre-cracking was performed in air at room temperature at 15 Hz using the step down procedure starting at 20 MPa.$\sqrt{m}$ and decreasing load to attain about 5 MPa.$\sqrt{m}$. Then the FCG tests started from 5 MPa.$\sqrt{m}$ at a frequency of 5 Hz and a stress ratio $R = 0.5$, at 300°C in air and in LBE.
The results shown in Figure 7.5.5 reveal a net increase in the fatigue crack growth rate for T91 in contact with LBE, in comparison with air, in agreement with the LCF results of Figures 7.5.1 and 7.5.2.

Figure 7.5.5. Fatigue crack growth curves for T91 at 300°C in air and in LBE (5 Hz, R = 0.5)

The above results are remarkable, owing to the common observation that LBE does not easily reach the crack tip. Intergranular penetration of the liquid metal is not a characteristic of the T91-LBE couple. In this system, crack opening is not immediately followed by filling with liquid metal, contrary to model systems like Cu-Bi or Ni-Bi [Wolski, 2002].

Moreover, for both studies devoted to FCG of MANET II and T91 in LBE, it is also worth remembering that the oxidising or reducing power of LBE was unknown in one case [Kalkhof, 2003], and that the LBE was oxidising in the other case [Verleene, 2006].

7.5.6 Influence of LBE on fatigue fracture surface morphology of T91

LBE influences the macroscopic fracture surface morphology and fracture mode as is illustrated in Figures 7.5.6 and 7.5.7. The following characteristics are observed:

- After LCF test of T91 in air [Figure 7.5.6(a)], the fracture surfaces are rather tortuous with a fracture surface at about 45° with respect to the loading axis. Multiple initiation sites, from which cracks propagated into the bulk, are observed. The fracture surface results from the junction of the various propagation planes, which entails a macroscopically inclined fracture.
- After LCF test of T91 in contact with LBE, without preliminary exposure to LBE, the fracture surface was rather flat with a unique crack initiation site [Figure 7.5.6(b)].
- After LCF test of T91 in contact with LBE, with preliminary exposure to LBE, the fracture surface was rather flat with several crack initiation sites.
At microscopic scale, some differences could be noticed between fracture surfaces in air and in LBE. However, fretting of the surface during the test made the SEM examinations rather difficult. Nevertheless, fatigue striations, typical of fatigue failure were observed in some situations.

- The striations, visible after LCF fracture in air, are enlarged as a result of LCF testing in LBE: about a few μm in air and possibly attaining ~100 μm in LBE.

- A change in the fracture mode was observed in the FCGR specimens, with a transition from ductile striations with small distances between them in air [Figure 7.5.7(a)] to a mixed brittle inter- and transgranular fracture in LBE [Figure 7.5.7(b)].

These results are in agreement with the acceleration of the FCG rate induced by LBE, and illustrated with Figure 7.5.5.

Figure 7.5.7. SEM micrographs of typical fatigue fracture surfaces, as a result of FCP tests of T91 (left) in air, and (right) in LBE
7.5.7 Influence of LBE on fatigue crack initiation in T91 and MANET II

For both MANET II and T91, the crack initiation mechanism is modified by contact with LBE, in comparison with air, as reported in [Kalkhof, 2003] and [Vogt, 2004], [Verleene, 2006].

For MANET II, a strong reduction in the number of cycles for fatigue crack initiation was observed at 260°C in LBE in comparison with air. This was discussed on the basis of metallographic observations.

The two crack initiation sites and cracks are shown in Figure 7.5.8. After LCF testing in air, a main crack and a number of short cracks coexist at the MANET II specimen surface, whereas one single crack remains in LBE, whose morphology contrasts with the one of the air-formed cracks. This main crack presents straight walls and lateral sub-cracks are filled with LBE.

Figure 7.5.8. Photomicrographs of MANET II specimens after LCF testing (top) in air and (bottom) in LBE. Note the fast crack propagation for MANET II in LBE compared to 316L in otherwise identical conditions.
Complementary information on the crack initiation mechanism is given by J-B. Vogt, *et al.* [Vogt, 2006], [Verleene, 2006]. Crack initiation was found to be transgranular in air and LBE alike. Cracks grow through the grains, occasionally at grain boundaries in LBE. In addition, the cracks exhibited the following characteristics:

- In air, the short cracks are generated by a classical extrusion-intrusion process.
- In LBE, the evolution of the population of cracks initiated in T91 specimens is similar to that represented in Figure 7.5.8 for MANET II.
- Preliminary exposure to reducing LBE leads to intergranular cracks; some of them will propagate during LCF testing, depending locally on the chemical and metallurgical conditions (Figure 7.5.9).

**Figure 7.5.9.** SEM micrographs of cross-sections of T91 specimens 613 h ageing in reducing LBE (<10⁻¹⁰ wt.% oxygen): a) before LCF testing and b) after LCF testing in LBE at 300°C, Δεₕ = 2.2%

For the T91-LBE couple, the distribution of cracks was analysed by J-B. Vogt, *et al.* [Vogt, 2006], [Verleene, 2006] as function of the imposed strain amplitude in LCF tests in both media (air, LBE) with the following observations:

- In air, the growth of grain-sized cracks is limited by the grain boundaries, which can be overcome after a certain number of cycles. Crack extension therefore occurs by crystallographic growth, which again is limited by other grain boundaries but the crack length attains now three or four grains sizes; longer microcracks can form by coalescence of smaller ones. Finally, only very few of them propagate in a plane perpendicular to the stress axis into the bulk. The role of the microstructure on crack growth in air was already published [Vogt, 1988].
- In LBE, the author suggests that once a microcrack forms inside a grain, the grain boundary resistance to crystallographic growth vanishes in contact with the liquid metal, allowing for crack extension throughout the neighbouring grains until final rupture.

It remains to explain why and how LBE facilitates the extension of the first crack embryo, and correlatively prevents the initiation of other cracks, at all scales (not only macroscopic, but also microscopic and sub-microscopic). Let us recall:

- that LBE is oxidising in the above-reported studies, except in the conditions of Figure 7.5.9;
- that the mechanism of transport of the embrittling atoms in a crack, at all stages of crack growth, is unknown;

306
that the mechanism of oxygen transport in a confined liquid medium like a grain boundary or a crack is unknown;

that the penetration of LMs at grain boundaries or into cracks has been treated recently by different authors, but that a unique model accounting for all experimental details is still missing.

7.5.8 **Low-cycle fatigue behaviour of 316L type stainless steel in contact with lead alloys, in comparison with lithium and sodium**

There is an abundant literature on compatibility of 316 type austenitic stainless steels with Pb-17Li and alkali metals like Li and Na. In this paragraph, we have deliberately selected a few papers summarising the information on LCF and FCG of austenitic steels in these media (see Table 7.5.1 in the annex to this chapter).

Once the differences due to the impurity content in the LMs (especially O, C and N), due to the testing procedure including pre-exposure effects, and the characteristics of the material (commercial heat, product form, initial heat treatment) are taken into account, it appears that the fatigue behaviour of austenitic stainless steels in sodium and lithium is superior to that in air [Chopra, 1983], and that the LCF behaviour of 316L is unaffected by contact with Pb-17Li [Benamati, 1994]. It was also reported that the FCG rate for 316LN in sodium is considerably lower than in air, with a threshold stress intensity factor being a function of the stress R-ratio [Mishra, 1997].

Recent results on the fatigue behaviour of 316LN stainless steels in mercury were published at ORNL [Strizak, 2001]. Mercury has no effect on the endurance limit. However, at higher stresses, for fully reversed traction-compression tests (R = -1), mercury reduces the fatigue life by a factor of 2-3 with respect to air. The influence of mercury also appeared to be frequency sensitive with a synergic effect. Fatigue lifetimes in Hg at 0.1 Hz were found to be approximately 70% lower than those at 10 Hz. The role of wetting by mercury on the fatigue life was also emphasised.

Turning now to the low-cycle fatigue behaviour of 316L stainless steel in stagnant LBE, the available data are largely consistent with the above-mentioned results [Kalhhofer, 2003]:

- Cyclic softening of 316L, as noted above for MANET II and T91, is found independent of the environment, air or LBE at 260°C.
- At low strain amplitude, $\varepsilon_{\mathrm{at}} = 0.3\%$, even attaining 0.5%, the fatigue life for 316L in LBE is comparable to that in air;
- At total strain amplitude $\varepsilon_{\mathrm{at}} \geq 0.5\%$, a weak influence of LBE was observed.

The only detrimental effect of LBE on LCF of 316L concerns the crack propagation, considered by the authors slightly faster in LBE than in air, at 260°C, for $\Delta \varepsilon_i = 0.3\%$, and 1 Hz cycle frequency (see Figure 7.5.2).

To conclude, as of this date, the influence of LBE on the LCF behaviour of 316L SS can be considered weak.
7.6 Creep properties: Definition and state of the art concerning the austenitic steel of type 316 and the ferritic/martensitic steel of type T91 in contact with lead and LBE

7.6.1 Definition

Creep of materials is associated with time-dependent plasticity under constant stress at elevated temperature, often larger than roughly 0.5 T_m with T_m being the absolute melting temperature. Either constant stress or constant strain rate conditions can be adopted. The micro-mechanisms controlling creep deformation involve dislocation glide and climb and also, at low stresses, diffusion controlled mass transport along grains boundaries.

Classically, the creep rate varies in between $10^{-7}$ h$^{-1}$ and $10^{-1}$ h$^{-1}$, depending on applied stress (from tens to a few hundred of MPa) and temperature. In specific cases, creep tests have been performed on creep machines allowing for creep rates $\dot{\varepsilon}$ as low as $10^{-9}$ h$^{-1}$. The creep data include the stress vs. time to rupture, the total elongation vs. time to rupture, the reduction of area vs. time to rupture as function of temperature, and also the evolution of the creep rate as function of temperature, under various applied stresses.

The creep strength is defined in terms of stress versus creep rate and is measured in stress relaxation tests lasting 24 hours.

7.6.2 Creep properties of martensitic and austenitic stainless steels in air or liquid metals other than lead or LBE

There is in the literature a substantial amount of creep data in air, on commercial heats of modified 9Cr-1Mo steels over a wide temperature range, from 425°C to ~700°C. These data were required to establish the effect of a number of metallurgical parameters like heat treatment, cold work, notch sensitivity, thermal ageing and applied stress. Irradiation creep of ferritic/martensitic steels was also thoroughly investigated using different reactors or in laboratory irradiation facilities [Klueh, 2001], [Toloczko, 1996]. The (interrupted) tests are followed by micro-structural investigations.

Today, the tempered martensitic Cr-steels are reputed for their quite stable microstructures and good mechanical properties at elevated temperatures thanks to the pinning of dislocations and lath interfaces by fine precipitates and elements in solid solution (Cr, Mo, C...) [Guttmann, 1997], [Hättestrand, 2001].

The 10^5 hours creep rupture strength of T91 steel at 600°C was measured to be of the order of 100 MPa [Boutard, 2001].

As noted above in Section 7.5 dedicated to fatigue and creep-fatigue behaviour, the creep behaviour of both martensitic and austenitic stainless steels in contact with Pb-17Li, lithium and sodium were studied in parallel, in the framework of the fast breeder reactors and fusion projects. Perhaps it could be an element of information to recall that there is no evidence of a deleterious influence of sodium on the creep properties of type 316 austenitic stainless steels. As concerns the influence of Pb-17Li on the creep properties of martensitic steels, one should refer to the review papers by H.U. Borgstedt and co-workers; once again a slight reduction of creep life was obtained in a number of experimental conditions.
7.6.3 Creep and creep crack growth of both austenitic and ferritic/martensitic steels in lead or LBE

There is almost no information on the creep strength, creep damage and creep crack growth rates of both T91 and 316L in contact with lead or LBE, referring to the available accessible literature. E.E. Glickman was the first to mention a detrimental effect of liquid metals on creep [Glickman, 1976, 1977, 1985, 2000]. At the end of the 70s, the author proposed an explanation, considering that liquid metal accelerated creep (LMAC) is one more manifestation of the Rebinder effect, besides LME. A study of 2004 reporting an LMAC effect on both the T91-lead and the T91-LBE couples is briefly described in Section 7.6.5. At the same period, in Russia, in the context of the BREST-0D-300 reactor system, creep tests were performed on a chromium steel 10Kh9NSMFB (containing 1.2%Si) in flowing liquid lead under 70, 100 MPa between 420 and 550°C, showing an earlier transition into the third stage of creep and a decrease of the duration of the steady creep stage, explained by the authors as a consequence of the lead corrosiveness [Kashtanov, 2004]. More detailed information about the test conditions and composition and structure of the steel/lead interface would be of interest at all stages of the test. This includes easier access to the Russian previous and present literature on structural materials in contact with liquid metals for nuclear applications [Balandin, 1961], [Bryant, 1988].

7.6.4 Liquid metal accelerated creep (LMAC)

An increase in the secondary creep rate, by a factor of 2 to 100, was reported for single and polycrystals of Zn, Cd, Cu, Fe and Fe-Ni alloy, tested under tensile or compressive stress in experiments performed in the former USSR [Glickman, 1976, 1978; Nikitin, 1967]. LMs accelerate, at the same time, creep and the nucleation growth of vacancy voids near the metal surface in traction or compression.

7.6.5 Accelerated plastic strain of T91 steel in contact with lead


The FLEXIMEL specimens are (4 mm × 50 mm × 1 mm) platelets inserted in an alumina specimen holder, which applies a fixed symmetric four-point bending. They can be annealed either in a liquid LM bath under OCS, or in gas atmosphere (air or pure H2). A constant deflection of 0.2 mm is imposed to the platelets between the central and outer bearings, which corresponds to an initial maximum stress of 135 MPa, about 25% of the yield stress at the imposed temperature of 525°C. During annealing in lead, LBE or in air at elevated temperature, the elastic energy stored is relaxed and activates plastic deformation mechanisms.

The test results are shown in Figures 7.6.1 and 7.6.2. The authors observed the formation of cavities and an acceleration of plastic strain in the T91 steel specimens under fixed four-point bending at 525°C in both reducing (oxygen activity: \(a_0 = 2.7 \times 10^{-16}\)) and oxidising (oxygen activity: \(a_0 = 3.1 \times 10^{-16}\)) lead or LBE, which is never observed at same temperature in air.

13 COXCIMEL: in French, “Corrosion sous OXygène Contrôlé et Interaction avec les MEtaux Liquides”, refers to an original oxygen control system (OCS) developed by V. Ghetta, et al. [Ghetta, 2001], which permitted to determine the values of the oxygen solubility in lead and LBE over the 250-700°C temperature range, in very good agreement with the results obtained by J.L. Courouau using a CEA made OCS device [Courouau, 2002, 2004].
14 FLEXIMEL: in French, “FLEXion sous OXygène Contrôlé et Interaction avec les MEtaux Liquides”, refers to an experimental set-up allowing for four-point bending test under the OCS developed earlier by V. Ghetta [Ghetta, 2002].
Figure 7.6.1. SEM micrographs of the FLEXIMEL specimen central cross-section after 1 month annealing in stagnant liquid lead bath at 525°C under Ln(a₀) = -16 oxygen activity: a) tensile zone; b) compressive zone

Figure 7.6.2. Volume fraction of cavities in the central cross-section of a FLEXIMEL specimen after 1 month annealing in stagnant liquid lead bath under flowing H₂ at 525 °C (image analysis)

Apparently no such LMAC effect is detected at 380°C, in otherwise identical conditions [Gamaoun, 2003]. The threshold temperature for appearance of an LMAC effect is still missing.

7.6.6 Creep crack growth of T91 and 316L in contact with LBE or lead

There are no data on creep crack growth for T91 or 316L in contact with LBE or lead.

7.7 Fracture mechanics: Case of both austenitic steel of type 316 and ferritic/martensitic steel of type T91 in contact with lead and LBE

There is a large body of literature devoted to the fracture of structural materials, hardened and often embrittled under irradiation, covering a wide range of experimental test conditions. Indeed, this is an information of primary importance, which, for example, allowed for an estimate of the service life of the MEGAPIE target [Dai, 2005].
There is no such information available for structural materials (both T91 and 316L) in contact with HLMs. It is sometimes stated that the ductile to brittle transition temperature, which may increase by approximately one hundred degrees after irradiation, should be only little increased due to contact with HLMs. This is pure conjecture, and must be verified experimentally.

7.8 Recommendations for testing procedures

We begin by listing some of the ASTM standards, which could be useful for mechanical tests in HLMs, in spite of the fact that none of them are valid in such LM environment. We continue with a brief summary of the possible experimental installations, pointing out the drawbacks for each of them. Then we present some recommendations for the mechanical testing procedures, emphasising all that concerns the surface state.

7.8.1 ASTM standards useful for mechanical tests in LBE

Strictly speaking, there is no ASTM standard rigorously applicable in HLM environment. However, we shall recall the ones giving some information useful for our activities.

**ASTM E 1457 – 98**

Standard test method for measurement of creep crack growth rates in metals.

**Aim:** Determination of creep crack growth rates in metals at elevated temperature using compact type C(T) specimens subjected to static loading. The crack growth rate \( \frac{da}{dt} \) is expressed in terms of the magnitude of a crack tip parameter \( C^*(t) \). For definitions of \( C^*(T) \), see Test.

Note that the surface crack length measurement by optical means is not, in principle, considered reliable as a primary but only as an auxiliary method, because of the possibly non-uniform crack extension across the thickness of the specimen.

**Table I. Some specifications and conditions of application of ASTM E 1457-98**

<table>
<thead>
<tr>
<th>Applicable</th>
<th>Restricted to materials in which crack growth is accompanied by accumulation of substantial time dependent creep strains at crack tip.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not applicable</td>
<td>If crack growth controlled by high temperature corrosion. In case of transition creep behaviour leading to transient crack growth behaviour. In case of wide spread creep damage at crack tip.</td>
</tr>
<tr>
<td>Specimens</td>
<td>C(T), M(T)(^1) possibly required: fatigue pre-cracking.</td>
</tr>
</tbody>
</table>

\(^1\) M(T) = centre cracked tension specimens. 
\(^2\) AK, the stress intensity factor range, can be calculated using equations in test method E 399. 
\(^3\) J-integral = line or surface integral describing the local stress-strain field around the crack front, as described in test method E 616.

**Concluding remarks:** Stricto sensu, the ASTM E1457-98 test is not applicable to quantify creep crack growth rates in case of structural materials in contact with corroding heavy liquid metals like lead and

311
a fortiori corroding LBE. Nevertheless, the recommendations mentioned in the test method E 1457 will be useful to determine qualitatively the creep crack growth rates of T91 steel wetted/corroded by lead or LBE, under various temperature and loading conditions.

**ASTM E 813 – 89 (discontinued 1998)**

Standard test method for $J_{IC}$, a measure of fracture toughness.

Aim: Determination of $J_{IC}$, which can be used as an engineering estimate of fracture toughness near the initiation of slow stable crack growth for metallic materials.

**Table II. Some specifications and conditions of application of ASTM E 813-89**

<table>
<thead>
<tr>
<th>Applicable</th>
<th>Not applicable</th>
</tr>
</thead>
<tbody>
<tr>
<td>To sufficiently ductile material.</td>
<td>In case of predominant environmentally assisted cracking.</td>
</tr>
<tr>
<td>Lacking sufficient thickness to be tested for $K_{IC}$ according to test method E 399.</td>
<td>In case of fast fracture, and especially brittle (cleavage) fracture of steels.</td>
</tr>
<tr>
<td>Displaying ductile slow stable crack growth at test temperature.</td>
<td></td>
</tr>
<tr>
<td>To evaluate the effects of metallurgical variables, heat treatments and weldments.</td>
<td></td>
</tr>
</tbody>
</table>

**Specimens**

- Containing notches or flaws, sharpened by fatigue cracks. Recommended: three-point bend specimen SE(B), or C(T) with slow loading rate.

**Referenced documents**

- E 399: Test method for fracture toughness of metallic materials.
- E 616: Terminology relating to fracture testing.
- E 1152: Test method for determining J-R curves.

1 $SE(B) = \text{single edge-cracked specimens of length } 0.5 \leq a/W \leq 0.75$
2 $\Delta K$, the stress intensity factor range, can be calculated using equations in test method E 399.
3 $J$-integral = line or surface integral describing the local stress-strain field around the crack front, as described in test method E 616. The $J_{IC}$ value is in principle independent of the testing speed in quasi-static regime. Its value becomes a function of testing speed in the dynamic regime.
4 Environmental attack under sustained stress or cyclic loading can cause crack extension at J values less than $J_{IC}$.

**Concluding remarks:** Stricto sensu, the ASTM E813-98 test is not applicable to determine the fracture toughness of structural materials in contact with heavy liquid metals like lead or LBE, especially in case wetting could cause sudden brittle failure. Nevertheless, the recommendations mentioned in the test method E 813 will be useful to determine qualitatively the resistance to crack growth of T91 steel wetted/corroded by lead or LBE, under various temperature and loading conditions.

**ASTM E 1820 – 99**

Standard test method for measurement of fracture toughness, combination of ASTM E 813 for $J_{IC}$ evaluation and ASTM E 1152 for J-R curve evaluation.

Aim: Determination of fracture toughness of metallic materials using the parameters K, J and CTOD ($\delta$). Assuming the presence of a pre-existing sharp fatigue crack, the fracture toughness values identified by this method characterises its resistance to: 1) fracture of a stationary crack; 2) fracture after some stable tearing; 3) stable tearing onset; 4) sustained stable tearing.

**Concluding remarks:** See those for test method E 813.

---

15 $J_{IC}$ designates the line or surface integral characterising the local stress-strain field around the crack tip, near the onset of stable crack growth.
Table III. Some specifications and conditions of application of ASTM E 1820-99

<table>
<thead>
<tr>
<th>Applicable</th>
<th>“When the material response cannot be anticipated before the test”. Useful as a basis for material comparison, selection and quality assurance. Useful as a basis for structural flaw tolerance assessment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimens</td>
<td>C(T), SE(B), DC(T)&lt;sup&gt;1&lt;/sup&gt;; Required: notches sharpened by fatigue cracks</td>
</tr>
</tbody>
</table>

<sup>1</sup> SE(B) = single edge bend; DC(T) = disk-shaped compact.<br><sup>2</sup> ΔK, the stress intensity factor range, can be calculated using equations in test method E 399<br><sup>3</sup> J-integral = line or surface integral describing the local stress-strain field around the crack front, as described in test method E 616.

**ASTM E 1921-05**

Standard test method for measurement of reference temperature T<sub>0</sub>, which characterises the fracture toughness of a steel that experiences onset of cleavage cracking at elastic, or elastic-plastic K<sub>Jc</sub> instabilities, or both.

**Aim:** Determination of fracture toughness of metallic materials using the parameter J in the transition temperature region.

Table IV. Some specifications and conditions of application of ASTM E 1921-05

<table>
<thead>
<tr>
<th>Applicability</th>
<th>To steel that fails by cleavage.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimens</td>
<td>C(T), SE(B), DC(T). Required: notches sharpened by fatigue cracks.</td>
</tr>
</tbody>
</table>

7.8.2 **Adaptation of experimental installations for HLMs**

1) Use an open crucible, containing the test specimen immersed in stagnant LM, which is located within an inert gas cell or glove box. Advantage: inexpensive to build and operate. Drawback: exposure to contaminants…

2) Use a circulating loop; CT and three-point bend specimens can be studied in such installation. The advantage is obvious in case of *in situ* testing; tests are generally conducted *post mortem*; this procedure is convenient provided the tests are conducted at the temperature of exposure to the flowing LM, with layers of liquid metal present on the specimen surface. Otherwise, one should be careful for interpretation of results obtained at room temperature.

3) Use sealed environmental chamber attached to the specimen, that completely surrounds the notch and crack extension plane for compact-type specimens, which contains the LM but does not extend to the region of the loading holes. Advantage: simple and low cost. Drawback: static LM…hence the characteristics of large heat-transport systems (e.g. mass transport due to non-isothermal operation) cannot be studied.

4) Controlled specimen preparation, using surface physics techniques, in order to wet, oxidise, protect or corrode the specimens, particularly notch or pre-cracked area. Advantage: possibility to follow (optically…) the damage evolution, well adapted to understand damage mechanisms. Drawback: impossible to reproduce the conditions of a liquid metal cooling system.
Other additional difficulty in case of conductive liquid metals in contact with conductive structure materials, electric potential methods cannot be adapted. To make a parallel, if one thinks to the electrochemic methods applicable to the study of stress corrosion cracking in aqueous environment, this is again a unique possibility to follow crack propagation that is lost in the case of HLMs like liquid lead or LBE.

For the future, the ultrasonic techniques recently developed to investigate the LM/steel interfaces would be of great interest [Lesueur, 2004].

7.8.3 Recommendations for testing procedures

Are concerned the steel surface and metallurgical preparation prior testing, testing procedure itself with relevant indications possibly given by ASTM standards, and post-test analysis of the specimens. All that concerns the metallurgical preparation prior testing, the heat treatment must be “standardised”. We concentrate on the surface preparation conditions and surface state prior and after mechanical testing. Contrary to what is considered mandatory for corrosion studies, OCS is not required for mechanical tests, provided the surface state is followed, using all possible surface analysis methods, over the whole test duration. This includes:

Prior mechanical test

1) Polishing conditions must be made precise: diamond-polishing should be preferred, knowing that electro-polishing is an efficient passivating treatment, which is not the case of manual polishing (SiC or diamond); coarse mechanical grinding should be avoided.

2) General aspect must be made precise: shiny if possible; in case of roughness: the presence of metallurgical defects like inclusions, scratches, presence, distribution and size of superficial pre-cracks (if possible) must be mentioned.

3) Ageing time and conditions (air, cover gas, LBE…) prior testing must be noted:
   - In case of air ageing, it is important to know precisely the ageing time, even if a few hours, since the native oxide on Cr containing steels is evolving very rapidly during the first 24 hours, the first week of ageing, which may have non negligible consequences on the mechanical resistance.
   - In case of direct immersion and ageing in liquid LBE, the oxygen activity in LBE and temperature must be known if possible, if different from that applied during testing.

During mechanical test

Except in some specific cases, in an opaque LM, it is not generally possible to follow the surface state. However, All accessible parameters must be known: temperature, duration of the different test phases, and oxygen content in LM, depending on the test (for slow strain rate tensile test if possible, for creep test and creep crack growth testing…).

During mechanical test, once a crack initiated, it would be important, ideally, to know how LBE fills the crack. It could be of interest to analyse some specimens obtained during interrupted tests. It should be important for creep, fatigue and creep-fatigue testing. This is a hard task, but which could be really helpful in order to interpret the obtained mechanical data, as far as LME or EAC effects are concerned.
The study of the compatibility of structural materials with heavy liquid metals (lead, lead-bismuth eutectic…) represents a non negligible contribution to the international research effort dedicated to the development of accelerator-driven systems and other innovative concepts of LM-cooled fast reactors concepts of Generation IV. It is worth recalling that compatibility means both corrosion and mechanical resistance, possibly in a radiation environment which should be the more representative of the nuclear facilities in project.

If one forgets deliberately the radiation environment, the problem is not so much simplified since the mechanical resistance is largely dependent on the corrosion properties of the system under study. It is worth recalling that the mechanical behaviour of a system will not be fully understood so long as the physicochemical processes occurring in contact with the selected HLM are not known in each experimental situation. They are varied, going from the corrosion-dissolution, corrosion-erosion, or oxide formation at the steel surface, to the formation of surface alloys with the reactive HLM in contact, to the formation of de-alloyed layers (possibly associated with the $\gamma \rightarrow \alpha$ phase transition of austenitic steels in contact with lead alloys) to the reactive or non reactive wetting depending on the miscibility of the solid and liquid phases in contact. In addition, if one recalls that a non-equilibrium steady state is only attainable for a material in contact with a corrosive HLM, one immediately observes that the mechanical resistance may change with the surface state, during ageing. This is certainly the reason why the Russian metallurgists, who can be considered as pioneers in this field, studied the mechanical properties of steels in contact with HLMs, taking two opposite orientations: either the intrinsic mechanical answer was obtained in conditions of direct contact between the two solid and liquid phases, by using the method of the soldering fluxes, or the mechanical answer was
followed in an HLM environment of controlled corrosiveness, thanks to the early development of the oxygen control systems in the former USSR. This orientation was caused by the corrosiveness of lead and lead alloys which may dissolve substantial amounts of oxygen with solubility limits largely varying between 250 and 600°C, i.e. in the temperature range of interest for the nuclear facilities in service or in project.

Another difficulty encountered in this chapter dedicated to the mechanical properties of structural materials in HLMs comes from the variety of the literature sources worldwide (in Russia, Japan, China, Korea…), with no translation, or only partial information available. Let us recall that when the European countries started to work on compatibility of lead and LBE with structural materials in the frame of the ADS project in 1997/1998, the crucial point was the absence of OCS…outside Russia, and the main question how to redevelop this technology. In 2004, the expression for the oxygen solubility limit in lead as function of temperature, proposed by Orlov, is rediscovered and discussed in EU, USA, Japan. In 2006, we are far from this state of the art as concerns the mechanical properties of Cr containing steels in contact with lead and LBE. The Russian expertise in this area is only very partially known… Apart from the absence of translation of an impressive literature, there is the problem of the steel grades developed in the former USSR, differing from the ones developed outside Russia. One knows that the corrosion properties of a steel is function not only of its major but also largely of the presence of its minor alloying elements. One also knows that the mechanical properties of a given steel grade in a HLM environment will be largely function of its composition, structure and microstructure, which were optimised for a specific application. Consequently, it is a fact that so long as the steel grades, in and outside Russia, will not be compared, not only for their corrosion behaviour but also for their mechanical properties in HLMs, one should be concerned by such a lack of information.

In this chapter, emphasis is put on the austenitic steel of type 316L and on the ferritic/martensitic steel of type T91, which were selected as structural materials for the European ADS project and MEGAPIE target. In such a review, not only the tensile and fatigue properties, but also the creep, the creep-fatigue and fracture properties of both austenitic and ferritic/martensitic steels in contact with lead, lead-bismuth eutectic should have been reported. At the end of this chapter, a certain number of points are noticeable. The study of the tensile properties of T91 in lead and LBE in various experimental conditions revealed that the T91-LBE, and certainly the T91-lead couples are embrittling. However, provided the surface state be protected by an oxide film remaining adherent to the steel surface during long term ageing, the risk of embrittlement should be largely minimised. The T91-LBE couple is also susceptible to EAC, after long-term ageing in reducing LBE. The embrittling character of both the 316L-lead and of the 316L-LBE couples remains to be proved. Fatigue is inherent to any structural component in service. The more significant effects of LBE on the fatigue behaviour of T91 are the following: there is a detrimental effect of LBE on the fatigue crack initiation resistance, vanishing at low strain amplitudes or low stress amplitudes. LBE modifies the mechanism of formation of long fatigue cracks. LBE increases the fatigue crack growth rate. The effect of surface roughness is very important. Corrosion of T91 by LBE, in the dissolution regime, provides defects that are ready to propagate by cyclic loading, provided LBE attains the crack tip. Once a short crack forms in T91 in contact with LBE, it rapidly propagates into the bulk. This entails the need to protect the steel surface. Oxygen in LBE gives rise to an oxide layer that limits the interaction of LBE with short cracks. To the contrary, the low cycle fatigue of 316L stainless steel is only little affected by LBE. Only a weak effect of LBE on the fatigue life was observed, which was not considered as the proof of an embrittling effect. An accelerated plastic strain is observed with T91 in contact with both oxidising and reducing lead or LBE under OCS at the temperature of 525°C. However information is still strongly missing about the creep behaviour of both T91 and 316L in contact with lead or LBE. Likewise, information is completely missing concerning the fracture behaviour of both 316L and T91 in lead and LBE, i.e. the evolution of the ductile to brittle transition temperature, of the fracture
toughness as function of the contact conditions with LBE. The crack growth R resistance curve or the J resistance curves to be determined as functions of the plastic deformation evidenced locally in the crack tip area are also missing.

To terminate this chapter, it is not uninteresting to remark the consensus between all metallurgists confronted to the problem of LME immediately arising when one studies the compatibility of structural materials with HLMs. Today, in absence of an accepted theory of LME, the susceptibility to LME of structural materials being deformed in HLMs is unpredictable. Consequently, to solve practical problems, it is necessary to conduct investigations under conditions imitating or at least approaching the service ones. In all cases, it is recommended to investigate in more details the relationship between the physico-chemical processes occurring at the interface and the deformation and failure of the material, which could be useful for the future development of a physical model of liquid- and solid-metal embrittlement. In the future, one should also establish the rules of the origin of cracks and of their development in the presence of liquid media and solid metal films under long static and cyclic loads, and under conditions of mechanical failure to be able to describe properly the cracking process, which is extremely necessary for solutions of practical problems.

This point of view was proposed in the USSR in 1987 by Popovich [Popovich, 1987]. From the point of view of this handbook, it remains valid twenty years later, especially for all that concerns the metallurgical and mechanical factors determining the formation and further evolution of a crack embryo in contact with a liquid metal!
REFERENCES


Kurata, Y., private communication.


Santarini, G., private communication.


Table 7.4.1. Tensile behaviour of smooth and notched specimens of T91 in HLMs, as function of specimen preparation

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{not}}$ (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Strain rate</th>
<th>Mechanical data (see definitions below)</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91</td>
<td>20</td>
<td>Smooth cylindrical specimen: 20 mm gauge length 4 mm diameter Normalised at 1050°C (1 h) Tempered at 750°C (1 h)</td>
<td>Air</td>
<td>$4\times 10^{-3}$ s$^{-1}$</td>
<td>$\sigma_{0.2} = 500$ MPa $\sigma_{TS} = 650$ MPa A(%) = 25</td>
<td>Ductile fracture surface.</td>
<td>[Verleene, 2006]</td>
</tr>
<tr>
<td>T91</td>
<td>300</td>
<td>Smooth cylindrical specimen: 20 mm gauge length 4 mm diameter Electro-polished Normalised at 1050°C (1 h) tempered at 750°C (1 h)</td>
<td>Air</td>
<td>$4\times 10^{-3}$ s$^{-1}$</td>
<td>$\sigma_{0.2} = 450$ MPa $\sigma_{TS} = 570$ MPa A(%) = 20</td>
<td>No pre-wetting procedure. No embrittlement of T91 by Pb under air. Ductile fracture surface.</td>
<td>[Legris, 2000]</td>
</tr>
<tr>
<td>T91</td>
<td>300</td>
<td>Smooth cylindrical specimen: 20 mm gauge length 4 mm diameter Electro-polished Normalised at 1050°C (1 h) tempered at 750°C (1 h)</td>
<td>Lead under air (no OCS)</td>
<td>$4\times 10^{-3}$ s$^{-1}$</td>
<td>$\sigma_{0.2} = 440$ MPa $\sigma_{TS} = 550$ MPa A(%) = 19</td>
<td>No pre-wetting procedure. No embrittlement of T91 by Pb under air. Ductile fracture surface.</td>
<td>[Legris, 2000]</td>
</tr>
<tr>
<td>T91</td>
<td>350</td>
<td>Smooth cylindrical specimen: 20 mm gauge length 4 mm diameter Electro-polished Normalised at 1050°C (1 h) tempered at 750°C (1 h)</td>
<td>Air</td>
<td>$10^{-4}$ s$^{-1}$</td>
<td>$\sigma_{0.2} = 350$ MPa $\sigma_{TS} = 520$ MPa A(%) = 22</td>
<td>No pre-wetting procedure. No embrittlement of T91 by Pb under air. Ductile fracture surface.</td>
<td>[Legris, 2000]</td>
</tr>
<tr>
<td>T91</td>
<td>350</td>
<td>Smooth cylindrical specimen: 20 mm gauge length 4 mm diameter Electro-polished Normalised at 1050°C (1 h) tempered at 750°C (1 h)</td>
<td>Lead under air (no OCS)</td>
<td>$10^{-4}$ s$^{-1}$</td>
<td>$\sigma_{0.2} = 350$ MPa $\sigma_{TS} = 520$ MPa A(%) = 22</td>
<td>No pre-wetting procedure. Same conclusions as above. Sole effect of hardening heat treatment: reduction of elongation to rupture. The fracture remains fully ductile.</td>
<td>[Legris, 2000]</td>
</tr>
<tr>
<td>T91</td>
<td>350</td>
<td>Notched specimen: notch of 0.5 mm depth and 0.25 mm root radius 20 mm gauge length 4 mm diameter Electro-polished Normalised at 1050°C (1 h) Tempered at 750°C (1 h)</td>
<td>Lead under air (no OCS)</td>
<td>$10^{-4}$ s$^{-1}$</td>
<td>$\sigma_{0.2} = 900$ MPa $\sigma_{TS} = 1250$ MPa A(%) = 15</td>
<td>No pre-wetting procedure. Same conclusions as above. Sole effect of notch: reduction of elongation to fracture. Ductile fracture surface.</td>
<td>[Legris, 2000]</td>
</tr>
<tr>
<td>T91</td>
<td>350</td>
<td>Notched specimen: as described above Normalised at 1050°C (1 h) Tempered at 500°C (1 h)</td>
<td>Air</td>
<td>$2 \mu$m/s</td>
<td>–</td>
<td>Same as above. Sole effect of notch: reduction of elongation to fracture. Ductile fracture surface.</td>
<td>[Legris, 2000]</td>
</tr>
<tr>
<td>T91</td>
<td>350</td>
<td>Notched specimen: as described above Normalised at 1050°C (1 h) Tempered at 500°C (1 h)</td>
<td>Lead under air (no OCS)</td>
<td>$2 \mu$m/s</td>
<td>–</td>
<td>Brittle (transgranular) fracture of hardened T91(by tempering at 500°C) in Pb, in spite of the presence of an oxide film on T91, confirmed by SEM.</td>
<td>[Legris, 2000]</td>
</tr>
</tbody>
</table>
### Table 7.4.1. Tensile behaviour of smooth and notched specimens of T91 in HLMs, as function of specimen preparation (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{test}}$ ($^\circ$C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Strain rate</th>
<th>Mechanical data (see definitions below)</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91</td>
<td>20</td>
<td>Notched specimen: notch of 0.5 mm depth and 0.20 mm root radius 20 mm gauge length 4 mm diameter Normalised at 1050°C (1 h) Tempered at 500°C (1 h)</td>
<td>Air</td>
<td>2 $\mu$m/s</td>
<td>$E_{\text{fracture}} = 4$ J</td>
<td>• The fracture surface of notched and hardened specimens tested in air and in Hg at 20°C is brittle, showing a transgranular fracture in both cases.</td>
<td>[Nicaise, 2001]</td>
</tr>
<tr>
<td>T91</td>
<td>20</td>
<td></td>
<td>Hg under air (no OCS)</td>
<td>2 $\mu$m/s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>260</td>
<td></td>
<td>Air</td>
<td>2 $\mu$m/s</td>
<td></td>
<td>• Ductile fracture in air.</td>
<td>[Nicaise, 2001]</td>
</tr>
<tr>
<td>T91</td>
<td>260</td>
<td></td>
<td>LBE under air (no OCS)</td>
<td>2 $\mu$m/s</td>
<td></td>
<td>• Brittle transgranular fracture of notched and hardened specimens at 260°C tested in LBE or in Sn.</td>
<td>[Legris, 2002]</td>
</tr>
<tr>
<td>T91</td>
<td>260</td>
<td></td>
<td>Sn under air (no OCS)</td>
<td>2 $\mu$m/s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>350</td>
<td>Notched specimen: notch of 0.5 mm depth and 0.20 mm root radius 20 mm gauge length 4 mm diameter Normalised at 1050°C (1 h) Tempered at 500°C (1 h)</td>
<td>Lead under air (no OCS)</td>
<td>2 $\mu$m/s</td>
<td>$E_{\text{fracture}} = 1.2$ J</td>
<td>• For notched and hardened specimens of T91 in contact with Pb in air, there is a ductility trough extending from 350 to 425°C for a displacement velocity of 2 $\mu$m/s.</td>
<td>[Vogt, 2002]</td>
</tr>
<tr>
<td>T91</td>
<td>375</td>
<td></td>
<td>Lead under air (no OCS)</td>
<td>2 $\mu$m/s</td>
<td>$E_{\text{fracture}} = 1.2$ J</td>
<td>• We shall see below that the ductility trough is function of the strain rate.</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>400</td>
<td></td>
<td>Lead under air (no OCS)</td>
<td>2 $\mu$m/s</td>
<td>$E_{\text{fracture}} = 1.6$ J</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>425</td>
<td></td>
<td>Lead under air (no OCS)</td>
<td>2 $\mu$m/s</td>
<td>$E_{\text{fracture}} = 3$ J</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>450</td>
<td></td>
<td>Lead under air (no OCS)</td>
<td>2 $\mu$m/s</td>
<td>$E_{\text{fracture}} = 3.5$ J</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>450</td>
<td></td>
<td>Air</td>
<td>2 $\mu$m/s</td>
<td>$E_{\text{fracture}} = 3.6$ J</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$E_{\text{fracture}}$: area under the load versus cross head-displacement curve.
Table 7.4.2. Tensile behaviour of notched specimens of T91 in LBE under vacuum or hydrogenated helium

<table>
<thead>
<tr>
<th>Material</th>
<th>T&lt;sub&gt;test&lt;/sub&gt; (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Strain rate</th>
<th>Mechanical data (see definitions below)</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91 300</td>
<td>15 mm gauge length 4 mm diameter Diamond polished</td>
<td>Vacuum</td>
<td>1.7 10&lt;sup&gt;-5&lt;/sup&gt; 3.0 10&lt;sup&gt;-4&lt;/sup&gt; 6.710&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>A* = 135, E&lt;sub&gt;neck&lt;/sub&gt; = 3.3 J, UTS = 1000 A* = 152, E&lt;sub&gt;neck&lt;/sub&gt; = 3.8 J, UTS = 1000 A* = 162, E&lt;sub&gt;neck&lt;/sub&gt; = 4.1 J, UTS = 1000</td>
<td></td>
<td>[Guerin, 2003]</td>
<td></td>
</tr>
<tr>
<td>T91 350</td>
<td>Notched specimen: V-shaped 60° notch of 0.6 mm depth and 0.25 mm root radius</td>
<td>Vacuum</td>
<td>1.7 10&lt;sup&gt;-5&lt;/sup&gt; 6.710&lt;sup&gt;-4&lt;/sup&gt; 6.710&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>A* = 128, E&lt;sub&gt;neck&lt;/sub&gt; = 3.2 J, UTS = 1010 A* = 150, E&lt;sub&gt;neck&lt;/sub&gt; = 3.6 J, UTS = 970 A* = 153, E&lt;sub&gt;neck&lt;/sub&gt; = 3.8 J, UTS = 970 A* = 141, E&lt;sub&gt;neck&lt;/sub&gt; = 3.4 J, UTS = 970</td>
<td>• No direct contact between T91 and LBE under present vacuum conditions. • Correlatively there is no observable degradation of the tensile behaviour.</td>
<td>[Guerin, 2003]</td>
<td></td>
</tr>
<tr>
<td>T91 350</td>
<td>Normalised at 1050°C (1 h) Tempered at 750°C (1 h)</td>
<td>Stagnant LBE under vacuum</td>
<td>1.7 10&lt;sup&gt;-5&lt;/sup&gt; 6.710&lt;sup&gt;-4&lt;/sup&gt; 6.710&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>A* = 142, E&lt;sub&gt;neck&lt;/sub&gt; = 3.45 J, UTS = 990 A* = 147, E&lt;sub&gt;neck&lt;/sub&gt; = 3.55 J, UTS = 985 A* = 143, E&lt;sub&gt;neck&lt;/sub&gt; = 3.5 J, UTS = 965 A* = 149, E&lt;sub&gt;neck&lt;/sub&gt; = 3.6 J, UTS = 845</td>
<td></td>
<td>[Guerin, 2003]</td>
<td></td>
</tr>
<tr>
<td>T91 300</td>
<td>15 mm gauge length 4 mm diameter Diamond polished</td>
<td>Stagnant LBE under He + 4%H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.7 10&lt;sup&gt;-5&lt;/sup&gt; 6.710&lt;sup&gt;-4&lt;/sup&gt; 6.710&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>A* = 120, E&lt;sub&gt;neck&lt;/sub&gt; = 2.7 J, UTS = 945 A* = 124, E&lt;sub&gt;neck&lt;/sub&gt; = 2.8 J, UTS = 935 A* = 134, E&lt;sub&gt;neck&lt;/sub&gt; = 3.2 J, UTS = 940 A* = 154, E&lt;sub&gt;neck&lt;/sub&gt; = 3.4 J, UTS = 880</td>
<td>• The degradation of the mechanical properties depends on the deformation rate against oxidation rate. • The ductility trough, visible on the plot of energy to rupture vs. strain rate is pronounced at 350°C. • At 300°C the minimum ductility is just attained at 1.7 10&lt;sup&gt;-5&lt;/sup&gt; mm s&lt;sup&gt;-1&lt;/sup&gt;.</td>
<td>[Guerin, 2003]</td>
<td></td>
</tr>
<tr>
<td>T91 350</td>
<td>Notched specimen: V-shaped 60° notch of 0.6 mm depth and 0.25 mm root radius</td>
<td>Stagnant LBE under He + 4%H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.7 10&lt;sup&gt;-3&lt;/sup&gt; 6.710&lt;sup&gt;-4&lt;/sup&gt; 6.710&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>A* = 132, E&lt;sub&gt;neck&lt;/sub&gt; = 3.0 J, UTS = 900 A* = 120, E&lt;sub&gt;neck&lt;/sub&gt; = 2.5 J, UTS = 900 A* = 116, E&lt;sub&gt;neck&lt;/sub&gt; = 2.6 J, UTS = 880 A* = 140, E&lt;sub&gt;neck&lt;/sub&gt; = 3.0 J, UTS = 870</td>
<td></td>
<td>[Guerin, 2003]</td>
<td></td>
</tr>
<tr>
<td>T91 400</td>
<td>Normalised at 1050°C (1 h) Tempered at 750°C (1 h)</td>
<td>Stagnant LBE under He + 4%H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.7 10&lt;sup&gt;-3&lt;/sup&gt; 6.710&lt;sup&gt;-4&lt;/sup&gt; 6.710&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>A* = 148, E&lt;sub&gt;neck&lt;/sub&gt; = 3.1 J, UTS = 840 A* = 148, E&lt;sub&gt;neck&lt;/sub&gt; = 3.3 J, UTS = 885 A* = 116, E&lt;sub&gt;neck&lt;/sub&gt; = 2.4 J, UTS = 870 A* = 126, E&lt;sub&gt;neck&lt;/sub&gt; = 2.8 J, UTS = 890</td>
<td></td>
<td>[Guerin, 2003]</td>
<td></td>
</tr>
</tbody>
</table>

A* = Maximum cross-head displacement divided by initial notch length (in %). 
E<sub>neck</sub> = area under the load versus cross head-displacement curve (J). 
UTS = maximum load divided by the initial notched section (2.8 mm diameter) (MPa).
Table 7.4.3. Tensile behaviour of smooth or rough T91 steel specimens in oxygen saturated LBE

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Strain rate</th>
<th>Mechanical data</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91</td>
<td>200</td>
<td>Cylindrical smooth specimen: 15 mm gauge length 4 mm diameter</td>
<td>Vacuum</td>
<td>1.7 $10^{-3}$</td>
<td>$\sigma_{0.2} = 540 \text{ MPa}$ $\sigma_{TS} = 675 \text{ MPa}$ $A(%) = 22 \pm 1$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T91</td>
<td>200</td>
<td>Diamond polishing Normalised at 1050°C (1 h) Tempered at 750°C (1 h)</td>
<td>Oxygen saturated LBE under vacuum</td>
<td>1.7 $10^{-3}$</td>
<td>$\sigma_{0.2} = 540 \text{ MPa}$ $\sigma_{TS} = 675 \text{ MPa}$ $A(%) = 23 \pm 1$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T91</td>
<td>300</td>
<td></td>
<td></td>
<td>3.3 $10^{-4}$</td>
<td>$\sigma_{0.2} = 540 \text{ MPa}$ $\sigma_{TS} = 650 \text{ MPa}$ $A(%) = 20 \pm 1$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T91</td>
<td>350</td>
<td></td>
<td></td>
<td>1.7 $10^{-2}$</td>
<td>$\sigma_{0.2} = 515 \text{ MPa}$ $\sigma_{TS} = 610 \text{ MPa}$ $A(%) = 20 \pm 1$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T91</td>
<td>300</td>
<td>Flat specimen: 5 $\times$ 1.5 $\times$ 0.75 mm³ in gauge section</td>
<td>Oxygen saturated LBE</td>
<td>$10^{-5}$</td>
<td>$\sigma_{0.2,300} = 420 \text{ MPa}$ $\sigma_{TS,300} = 550 \text{ MPa}$ $\sigma_{crtk,300} \approx 400 \text{ MPa}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T91</td>
<td>375</td>
<td>Prepared by EDM cutting + electropolishing + mechanical polishing</td>
<td></td>
<td>$10^{-5}$</td>
<td>$\sigma_{0.2,375} = 400 \text{ MPa}$ $\sigma_{TS,375} = 550 \text{ MPa}$ $\sigma_{crtk,375} \approx 350 \text{ MPa}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>316L</td>
<td>200</td>
<td>Supplied by SIDERO STAAL (heat 744060) solution annealed + some cold work 12 mm gauge length 2.40 mm diameter</td>
<td>Air reference</td>
<td>$5 \times 10^{-6}$</td>
<td>$\sigma_{0.2} = 510 \text{ MPa}$ $\sigma_{TS} = 550 \pm 10 \text{ MPa}$ $\sigma_{crtk} \approx 340 \pm 10 \text{ MPa}$ $A(%) = 22 \pm 1$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>316L</td>
<td>200</td>
<td>Specimen in autoclave with gas conditioning system: LBE under Ar + 5%H₂ bubbling (4 h)</td>
<td></td>
<td>$5 \times 10^{-6}$</td>
<td>$\sigma_{0.2} = 550 \text{ MPa}$ $\sigma_{TS} = 580 \pm 10 \text{ MPa}$ $\sigma_{crtk} \approx 340 \pm 10 \text{ MPa}$ $A(%) = 22 \pm 2$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>316L</td>
<td>200</td>
<td>As above + final conditioning to obtain $10^{-8}$ wt.%. Oxygen dissolved in LBE</td>
<td></td>
<td>$5 \times 10^{-6}$</td>
<td>$\sigma_{0.2} = 550 \text{ MPa}$ $\sigma_{TS} = 580 \pm 10 \text{ MPa}$ $\sigma_{crtk} \approx 340 \pm 10 \text{ MPa}$ $A(%) = 21 \pm 2$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

- On smooth oxidised specimens of T91, LBE has no detrimental influence on the tensile behaviour at 300°C. See [Legris, 2000].
- Electro-polishing not only removes the flaws produced as a result of EDM cutting but also passivates efficiently the T91 steel specimens. Consequently electropolishing may prevent a possible embrittling effect of LBE.
- The authors hypothesis is that an intimate SM/LM contact is obtained thanks to the cracks forming spontaneously in the “brittle interfacial oxide” as a result of the conditioning system in autoclave. Slow strain rate tensile behaviour of 316L at 200°C is unmodified as a result of exposure to LBE, oxygenated or not, in present experimental conditions, according to the authors.

[Pastol, 2002]
[Dai, 2006]
[Sapundjiev, 2006]
Table 7.4.3. Tensile behaviour of smooth or rough T91 steel specimens in oxygen saturated LBE (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Strain rate (s⁻¹)</th>
<th>Mechanical data</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91 200</td>
<td></td>
<td>Supplied by UGINE (heat 36224) Normalised at 1040°C (1 h) Tempered at 760°C (1 h) 10 mm gage length 2.45 mm diameter</td>
<td>Air reference</td>
<td>5 × 10⁻⁶</td>
<td>(\sigma_{0.2} = 470) MPa (\sigma_{TS} = 610) MPa A(%) = 21 ± 1</td>
<td>• SSRT behaviour of T91 at 200°C is unmodified due to exposure to LBE, oxygenated or not, in present experimental conditions, according to the authors. • The authors suggested that the auto-repair of the cracked oxide film could explain the results, even at 200°C. • The authors confirmed their findings under controlled reducing environment. Comparable result were found for T91 in LBE at 250°C (see above).</td>
<td>[Sapundjiev, 2006]</td>
</tr>
<tr>
<td>T91 200</td>
<td></td>
<td>LBE under Ar + 5%H₂ bubbling (4 h)</td>
<td></td>
<td>5 × 10⁻⁶</td>
<td>(\sigma_{0.2} = 470) MPa (\sigma_{TS} = 600) MPa A(%) = 22 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91 200</td>
<td></td>
<td>As above + final conditioning to obtain 10⁻⁸ wt.% Oxygen dissolved in LBE</td>
<td></td>
<td>5 × 10⁻⁶</td>
<td>(\sigma_{0.2} = 470) MPa (\sigma_{TS} = 600) MPa A(%) = 20 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91 245</td>
<td></td>
<td>Normalised at 1040°C (1 h) Tempered at 760°C (1 h) 10 mm gage length 2.45 mm diameter</td>
<td>Ar + 5%H₂</td>
<td>5 × 10⁻⁶</td>
<td>(\sigma_{0.2} = 460) MPa (\sigma_{TS} = 600) MPa A(%) = 21 ± 1</td>
<td></td>
<td>[Sapundjiev, 2006]</td>
</tr>
<tr>
<td>T91 245</td>
<td></td>
<td></td>
<td></td>
<td>10⁻⁵</td>
<td>(\sigma_{0.2} = 440) MPa (\sigma_{TS} = 520) MPa A(%) = 21 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91 245</td>
<td></td>
<td></td>
<td></td>
<td>5 × 10⁻⁵</td>
<td>(\sigma_{0.2} = 440) MPa (\sigma_{TS} = 520) MPa A(%) = 21 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91 245</td>
<td></td>
<td></td>
<td></td>
<td>10⁻⁴</td>
<td>(\sigma_{0.2} = 440) MPa (\sigma_{TS} = 520) MPa A(%) = 21 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91 245</td>
<td></td>
<td></td>
<td></td>
<td>10⁻³</td>
<td>(\sigma_{0.2} = 440) MPa (\sigma_{TS} = 520) MPa A(%) = 23 ± 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7.4.3. Tensile behaviour of smooth or rough T91 steel specimens in oxygen saturated LBE (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Strain rate (s⁻¹)</th>
<th>Mechanical data</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| T91 245 |        | Normalised at 1040°C (1 h) Tempered at 760°C (1 h) 10 mm gage length 2.45 mm diameter | LBE under Ar + 5%H₂ | $10^{-5}$ | $\sigma_{0.2} = 490$ MPa  
$\sigma_{Y} = 630$ MPa  
A(%) = 18 ± 1 | • Coarse mechanical grinding.  
• No significant effect of strain rate on tensile properties of T91 in LBE at 245°C.  
• This result could be explained by the surface state, its roughness not allowing for intimate contact with the LM and hindering its possibly detrimental effect on the mechanical behaviour. | [Sapundjiev, 2006] |
| T91 245 |        |                                          | LBE under Ar + 5%H₂ | $5 \times 10^{-5}$ | $\sigma_{0.2} = 500$ MPa  
$\sigma_{Y} = 630$ MPa  
A(%) = 18 ± 1 | • Slight effect of strain rate observed in LBE at 450°C.  
• The main question remains in all cases: how to be sure that the initial cracks are filled by the liquid metal when no LM effect is detected, since post-mortem chemical analysis of the cracked zone is the only possible verification method? | [Sapundjiev, 2006] |
| T91 245 |        | Normalised at 1040°C (1 h) Tempered at 760°C (1 h) 10 mm gage length 2.45 mm diameter | LBE under Ar + 5%H₂ | $10^{-4}$ | $\sigma_{0.2} = 535$ MPa  
$\sigma_{Y} = 630$ MPa  
A(%) = 17 ± 1 | • Slight effect of strain rate observed in LBE at 450°C.  
• The main question remains in all cases: how to be sure that the initial cracks are filled by the liquid metal when no LM effect is detected, since post-mortem chemical analysis of the cracked zone is the only possible verification method? | [Sapundjiev, 2006] |
Table 7.4.4. Tensile behaviour of T91 in oxygen saturated LBE, in the presence of a random distribution of flaws in the specimens

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{tensile}}$ (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Strain rate ($s^{-1}$)</th>
<th>Mechanical data</th>
<th>Remarks</th>
</tr>
</thead>
</table>
| T91      | 250                       |                                       |                                 | $10^{-5}$              | $\sigma_{0.2,250} = 450$ MPa  
$\sigma_{TS,250} = 580$ MPa  
$\sigma_{\text{crack,250}} = 525$ MPa | • The distribution of cracks due to EDM cutting justifies the tensile behaviour. |
| T91      | 275                       |                                       |                                 | $10^{-5}$              | $\sigma_{0.2,275} = 420$ MPa  
$\sigma_{TS,275} = 570$ MPa  
$350 \leq \sigma_{\text{crack,275}} \leq 420$ MPa | • The filling of these cracks with LBE, competing with the oxide film formation on crack walls and at crack tip explains the spread in the stress versus elongation curves as function of temperature and exposure time in LBE. |
| T91      | 300                       | Flat specimen: 5 $\times$ 1.5 $\times$ 0.75 mm$^3$ in gauge section | Oxygen-saturated LBE at 300°C | $10^{-5}$              | $\sigma_{0.2,300} = 450$ MPa  
$\sigma_{TS,300} = 580$ MPa  
$420 \leq \sigma_{\text{crack,300}} \leq 525$ MPa | • There is no pronounced temperature effect on crack propagation. Same for ageing in LBE. |
| T91      | 325                       | Prepared by EDM cutting + mechanical polishing |                                 | $10^{-5}$              | $\sigma_{0.2,325} = 450$ MPa  
$\sigma_{TS,325} = 560$ MPa  
$475 \leq \sigma_{\text{crack,325}} \leq 540$ MPa | • At such slow strain rate ($10^{-5}$), oxygen diffusion in cracks is not controlling the cracking process. Passivation of cracks may occur. |
| T91      | 350                       |                                       |                                 | $10^{-5}$              | $\sigma_{0.2,350} = 430$ MPa  
$\sigma_{TS,350} = 570$ MPa  
$400 \leq \sigma_{\text{crack,350}} \leq 550$ MPa | • Crack propagation occurs apparently at random. |
| T91      | 375                       |                                       |                                 | $10^{-5}$              | $\sigma_{0.2,375} = 400$ MPa  
$\sigma_{TS,375} = 550$ MPa  
$360 \leq \sigma_{\text{crack,375}} \leq 520$ MPa | • The distribution of cracks, due to EDM cutting and the stress-strain state over the gage length of the specimens are undetermined. |
| T91      | 400                       |                                       |                                 | $10^{-5}$              | $\sigma_{0.2,400} = 430$ MPa  
$\sigma_{TS,400} = 530$ MPa  
$300 \leq \sigma_{\text{crack,400}} \leq 400$ MPa | • To explain why the “LBE embrittling effect” is not always observable, one should know the distribution of cracks and which ones are filled with LBE, which can only be determined post-mortem. |
| T91      | 425                       |                                       |                                 | $10^{-5}$              | $\sigma_{0.2,425} = 400$ MPa  
$\sigma_{TS,425} = 500$ MPa  
$300 \leq \sigma_{\text{crack,425}} \leq 400$ MPa | • Fracture surface: found brittle, when T91 is put into contact with LBE. |

[Dai, 2006]
Table 7.4.5. Tensile behaviour of T91 as a function of preliminary corrosion test conditions

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Preliminary corrosion test conditions</th>
<th>Tensile test conditions</th>
<th>Strain rate (s⁻¹)</th>
<th>Tensile properties</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MANET II</td>
<td>180</td>
<td>Flat tensile specimen: geometry adapted for LiSoR test section: 1 mm thickness, 20 mm gauge length, 5 mm width and 35 mm between shoulders</td>
<td>As received</td>
<td>Under argon</td>
<td>10⁻⁴</td>
<td>σ₀₂₀ = 580 MPa, σ₂₀ = 700 MPa</td>
<td>Loss of ductility at 250 and 300°C in LBE.</td>
<td>[Glasbrenner, 2003]</td>
</tr>
<tr>
<td>MANET II</td>
<td>200</td>
<td>As received Under argon</td>
<td>2 hours exposure in LiSoR loop at tensile test temperature</td>
<td>Under flowing LBE (LiSoR loop)</td>
<td>10⁻⁴</td>
<td>σ₀₂₀ = 580 MPa, σ₂₀ = 660 MPa</td>
<td>Mixed fracture surface: some flat areas and others showing dimples.</td>
<td></td>
</tr>
<tr>
<td>MANET II</td>
<td>250</td>
<td>Normalised at 1075°C (30 min) Tempered at 750°C (2 h)</td>
<td>As received</td>
<td>Under argon</td>
<td>10⁻⁴</td>
<td>σ₀₂₀ = 580 MPa, σ₂₀ = 670 MPa</td>
<td>These results could be surprising, considering that LBE is oxygen saturated in LiSoR.</td>
<td></td>
</tr>
<tr>
<td>MANET II</td>
<td>300</td>
<td>As received Under argon</td>
<td>3.10⁻³</td>
<td></td>
<td>10⁻⁴</td>
<td>σ₀₂₀ = 540 MPa, σ₂₀ = 600 MPa</td>
<td>Loss of ductility at 250 and 300°C in LBE.</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>400</td>
<td>Cylindrical specimen: 15 mm gauge length 3 mm diameter Normalised at 1040°C (1 h) Tempered at 760°C (1 h)</td>
<td>As received</td>
<td>Under argon</td>
<td>3.10⁻³</td>
<td>σ₀₂₀ = 535 ± 42 MPa, σ₂₀ = 645 ± 26 MPa A(%) = 22 ± 1 RAZ(%) = 72 ± 2</td>
<td>No clear effect of pre-exposure to LBE on yield stress and ultimate tensile stress, as already mentioned in LME review papers, except for the elongation to rupture (A) and reduction of area (RAZ).</td>
<td>[Fazio, 2003] [Aiello, 2004]</td>
</tr>
<tr>
<td>T91</td>
<td>400</td>
<td>1500 hours in LECOR loop at 400°C</td>
<td></td>
<td>Under argon</td>
<td>3.10⁻³</td>
<td>σ₀₂₀ = 535 ± 10 MPa, σ₂₀ = 640 ± 14 MPa A(%) = 18 ± 1 RAZ(%) = 42 ± 8</td>
<td>A clear effect of pre-exposure to LBE at 450°C.</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>400</td>
<td>4500 hours in LECOR loop at 400°C</td>
<td></td>
<td>Under argon</td>
<td>3.10⁻³</td>
<td>σ₀₂₀ = 515 ± 7 MPa, σ₂₀ = 625 ± 15 MPa A(%) = 16 ± 1 RAZ(%) = 32 ± 12</td>
<td>A loss of ductility is observed at the periphery of the fracture surface, which exhibits a flat morphology.</td>
<td>[Aiello, 2004]</td>
</tr>
<tr>
<td>T91</td>
<td>450</td>
<td>Normalised at 1040°C (1 h) Tempered at 760°C (1 h) 10 mm gage length 2.45 mm diameter</td>
<td>No pre-exposure to LBE Stagnant LBE under Ar + 5%H₂</td>
<td></td>
<td>5.10⁻³</td>
<td>σ₀₂₀ = 430 MPa, σ₂₀ = 450 MPa σ_fatigue = 250 MPa</td>
<td>Possible but not clear effect of pre-exposure to LBE at 450°C.</td>
<td>[Sapundjiev, 2006]</td>
</tr>
<tr>
<td>T91</td>
<td>450</td>
<td>4000 hours in stagnant LBE at 450°C</td>
<td>Stagnant LBE under Ar + 5%H₂</td>
<td></td>
<td>5.10⁻³</td>
<td>σ₀₂₀ = 400 MPa, σ₂₀ = 470 MPa σ_fatigue = 210 Mpa</td>
<td>Fracture surface aspect unknown.</td>
<td></td>
</tr>
</tbody>
</table>

Note: T = temperature, Specimen preparation and heat treatment, Preliminary corrosion test conditions, Tensile test conditions, Strain rate (s⁻¹), Tensile properties, Remarks, Ref.
Table 7.4.5. Tensile behaviour of T91 as a function of preliminary corrosion test conditions (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Preliminary corrosion test conditions</th>
<th>Tensile test conditions</th>
<th>Strain rate (s⁻¹)</th>
<th>Tensile properties</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| T91 380  |       | Cylindrical smooth specimen; 15 mm gauge length 4 mm diameter | 1 month exposure to LBE under OCS in reducing conditions: 3.5 10⁻¹¹ O₂ in COXCIMEL device [Ghetta, 2001, 2002] + relaxation test at 494 MPa under He | Under He | 4.5 10⁻⁵ | \(\sigma_{0.2} = 500 \text{ MPa} \)  
\(\sigma_{TS} = 560 \text{ MPa} \)  
A(%) = 20 | Cavitation effects in T91, as a result of prior ageing in COXCIMEL at 525°C, do not affect significantly the tensile behaviour at 380°C. | [Ghetta, 2001, 2002] |
| T91 380  |       | Normalised at 1050°C (1 h) Tempered at 750°C (1 h) | 1 month exposure to LBE under OCS in reducing conditions: 3.5 10⁻¹¹ O₂ in COXCIMEL device [Ghetta, 2001, 2002] + relaxation test at 494 MPa in LBE under He | Stagnant LBE under He | 4.5 10⁻⁵ | \(\sigma_{0.2} = 500 \text{ MPa} \)  
\(\sigma_{TS} = 550 \text{ MPa} \)  
A(%) = 19.3 | Specimens coated by LBE (coating possibly favoured by the presence of zinc traces), in which case brittle fracture is observed. | [Gamaoun, 2003, 2004] |
Table 7.4.6. Tensile behaviour of T91, in air, at room temperature, after exposure to lead or LBE

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Preliminary corrosion test conditions</th>
<th>Tensile test conditions</th>
<th>Strain rate (s(^{-1}))</th>
<th>Tensile properties</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91</td>
<td>T(_{\text{room}})</td>
<td></td>
<td>As received</td>
<td>Air</td>
<td>4.5 \times 10^{-5}</td>
<td>(\sigma_{0.2, \text{room}} = 460 \text{ MPa}) (\sigma_{T25, \text{room}} = 760 \text{ MPa}) A(%) = 27.3</td>
<td>No effect of preliminary exposure of tensile specimen for 1 month or six months in COXCIMEL device under OCS in reducing conditions when the specimens are tensile tested at room temperature.</td>
<td>[Gamaoun, 2003]</td>
</tr>
<tr>
<td>T91</td>
<td>T(_{\text{room}})</td>
<td>1 month exposure to LBE under OCS in reducing conditions: (3.5 \times 10^{-11} \text{ O}_2) in COXCIMEL device</td>
<td>Air</td>
<td>4.5 \times 10^{-5}</td>
<td>(\sigma_{0.2, \text{room}} = 460 \text{ MPa}) (\sigma_{T25, \text{room}} = 760 \text{ MPa}) A(%) = 29.8</td>
<td>• This result contrasts markedly with the ones obtained using four-point bending tests carried out in LBE under OCS at high temperature (500-525°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>T(_{\text{room}})</td>
<td>Cylindrical smooth specimen: 15 mm gauge length 4 mm diameter Normalised at 1050°C (1 h) Tempered at 750°C (1 h)</td>
<td>As received</td>
<td>Air</td>
<td>1.7 \times 10^{-3}</td>
<td>(\sigma_{0.2} = 565 \text{ MPa}) (\sigma_{T25} = 730 \text{ MPa}) A(%) = 26 ± 1</td>
<td>Surface state: Passive.</td>
<td>[Pastol, 2002]</td>
</tr>
<tr>
<td>T91</td>
<td>T(_{\text{room}})</td>
<td>12 h exposure to LBE under He-4%H(_2) (no OCS) at 150°C</td>
<td>Air</td>
<td>1.7 \times 10^{-3}</td>
<td>(\sigma_{0.2} = 565 \text{ MPa}) (\sigma_{T25} = 730 \text{ MPa}) A(%) = 26 ± 1</td>
<td></td>
<td>Surface state: roughened by corrosion at sub-micrometer scale.</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>T(_{\text{room}})</td>
<td>12 h exposure to LBE under He-4%H(_2) (no OCS) at 300°C</td>
<td>Air</td>
<td>1.7 \times 10^{-3}</td>
<td>(\sigma_{0.2} = 565 \text{ MPa}) (\sigma_{T25} = 730 \text{ MPa}) A(%) = 26 ± 1</td>
<td></td>
<td>Surface state: partial wetting.</td>
<td>[Pastol, 2002]</td>
</tr>
<tr>
<td>T91</td>
<td>T(_{\text{room}})</td>
<td>12 h exposure to LBE under He-4%H(_2) (no OCS) at 600°C</td>
<td>Air</td>
<td>1.7 \times 10^{-3}</td>
<td>(\sigma_{0.2} = 565 \text{ MPa}) (\sigma_{T25} = 700 \text{ MPa}) A(%) = 26 ± 1</td>
<td></td>
<td>Surface state: partially and locally wetted by LBE and locally corroded.</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>T(_{\text{room}})</td>
<td>12 h exposure to LBE under He-4%H(_2) (no OCS) at 650°C</td>
<td>Air</td>
<td>1.7 \times 10^{-3}</td>
<td>(\sigma_{0.2} = 565 \text{ MPa}) (\sigma_{T25} = 700 \text{ MPa}) A(%) = 26 ± 1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7.4.7. Tensile behaviour of T91 in conditions of direct contact with Pb-Bi

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen and heat treatment</th>
<th>Specimen preparation</th>
<th>Strain rate (s⁻¹)</th>
<th>Mechanical data</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91 350</td>
<td></td>
<td>Cylindrical smooth specimen</td>
<td>Diamond polishing to 1 μm, tested in air</td>
<td>10⁻⁵</td>
<td>σ₀.² = 380 MPa, σ₇₀ = 550 MPa, σₙₙₙₙ = 400 MPa, A(%) = 23</td>
<td>The size of the reservoir of Pb-Bi determines the overall tensile behaviour of T91 at 350°C. This explains the slight degradation of the parameters derived from the tensile tests in the case of the present Pb-Bi deposit, by comparison with reference tests in air. Brittle fracture surface at the specimen periphery, over the whole cracked areas attained by LBE in present conditions (temperature, surface state and stress-strain state of the cracked zones) [Auger, 2004, 2005]</td>
</tr>
<tr>
<td>T91 350</td>
<td></td>
<td>Normalised at 1050°C, Tempered at 750°C; 15 mm gauge length, 4 mm diameter</td>
<td>Diamond polishing to 1 μm, removal of native oxide by krypton ion sputtering + deposit of Pb-Bi layers (few hundreds of nm) onto the steel surface by PVD under UHV</td>
<td>10⁻⁵</td>
<td>σ₀.² = 380 MPa, σ₇₀ = 530 MPa, σₙₙₙₙ = 400 MPa, A(%) = 20</td>
<td></td>
</tr>
</tbody>
</table>
### Table 7.4.8. Embrittlement of martensitic steels in contact with other liquid metals or alloys: lithium and lead-lithium

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{test}}$ (^{\circ}\text{C})</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Strain rate ((\text{s}^{-1}))</th>
<th>Mechanical data ((\text{see definitions below}))</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4914</td>
<td>250</td>
<td></td>
<td>Air</td>
<td>2.78 (10^{-2}) (50 mm/min) 5.56 (10^{-4}) (1 mm/min)</td>
<td>$\sigma_{0.2} = 590-620$ MPa  $\sigma_{YS} = 680$ MPa RAZ(%) = 68</td>
<td>• No effect if exposure to lithium is followed by tensile test in air. See [Aiello, 2004]. • Corrosive attack caused by pre-exposure to lithium. • The so-formed cracks enlarge during tensile test in air, with no consequence on bulk properties.</td>
<td>[Borgstedt, 1986]</td>
</tr>
<tr>
<td>1.4914</td>
<td>250</td>
<td>Cylindrical smooth specimen: 30 mm gauge length 3 mm diameter Normalised at 1050°C (30 min) Tempered at 700°C (120 min)</td>
<td>Pre-exposure to lithium for 1000 h at 550°C prior tensile test in air</td>
<td>5.56 (10^{-4}) (1 mm/min)</td>
<td>RAZ(%) = 65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4914</td>
<td>200 &amp; 250</td>
<td></td>
<td>Lithium: purified to avoid variations of reactivity: &lt; 5 ppm wt. carbon &lt; 200 ppm wt. nitrogen O and H contents undetermined</td>
<td>2.78 (10^{-2}) (50 mm/min)</td>
<td>$\sigma_{0.2} = 540-590$ MPa  $\sigma_{YS} = 650$ MPa RAZ(%) = 49 (250°C) RAZ(%) = 43 (200°C)</td>
<td>• Embrittling effect of lithium at 200 or 250°C, with and without pre-exposure to lithium. • Influence of surface quality produced by machining emphasised: – machining marks – formation of minimum notches inducing an additional stress on the surface. – these notches act as incipient cracks that will propagate under the influence of stress and liquid metal.</td>
<td>[Borgstedt, 1986]</td>
</tr>
<tr>
<td>1.4914</td>
<td>200 &amp; 250</td>
<td></td>
<td>Exposure to lithium for 1000 h at 550°C prior tensile test in lithium</td>
<td>5.56 (10^{-4}) (1 mm/min)</td>
<td>RAZ(%) = 33</td>
<td>• Mixed fracture mode consisting of brittle inter-crystalline cleavage fracture and ductile shear fracture with flat and distorted dimples.</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>( T_{\text{test}} ) (°C)</td>
<td>Specimen preparation and heat treatment</td>
<td>Environmental testing conditions</td>
<td>Strain rate (s(^{-1}))</td>
<td>Mechanical data</td>
<td>Remarks</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
<td>----------------------------------</td>
<td>--------------------------------</td>
<td>-----------------</td>
<td>----------------</td>
<td>---------</td>
<td></td>
</tr>
</tbody>
</table>
| HT9      | 273 to 454      | Cylindrical smooth specimen: 10.2 mm gauge length 2.54 mm diameter Normalised at 1050°C (30 min) Tempered at 700°C (120 min) | Exposure to Pb-17Li for 18 h at 427°C to obtain “complete wetting” prior tensile test in Pb-17%Li (< 10 ppm wt. nitrogen 22 ppm wt. hydrogen) | 5.1 \times 10^{-6} 10^{-3} 10^{-2} | \( \sigma_{0.2} \approx 400 \), \( \sigma_{0.2,\text{air}} \leq 500 \) 490 \leq \sigma_{0.2,\text{PbLi}} \leq 560 600 \leq \sigma_{TS,\text{air}} \leq 660 600 \leq \sigma_{TS,\text{PbLi}} \leq 750 50 \times \text{RAZ} \leq 80 | • Dissolution rate of HT9 and 9Cr-1Mo steel in Pb-17Li ~2 to 5 times lower than for 316L: 0.4 \leq \text{dissolution rate} \leq 9 \text{ mg/m}^2 \times \text{h}.  
• No effect of Pb-17Li on tensile properties of HT9.  
• No visible corrosion effects or surface cracks on gauge surface.  
• Ductile dimpled fracture in all cases.  
[Chopra, 1986] |

| F82H-mod | 250             | For reference specimens tested in vacuum: additional heat treatment at 500°C for 15 h in vacuum | 1.1 \times 10^{-4} 0.1 \text{ mm/min} | \( \sigma_{0.2} = 559 \text{ MPa} \) \( \sigma_{TS} = 559 \text{ MPa} \) \( \text{A(\%) = 15} \) | \( \sigma_{0.2} = 502 \text{ MPa} \) \( \sigma_{TS} = 502 \text{ MPa} \) \( \text{A(\%) = 13.2} \) | • No embrittling effect of Pb-17Li on F82H-mod and OPTIFER IVb in present testing conditions: tensile behaviour unaffected with respect to air reference and (fully dimpled) fracture surface.  
• Assuming complete pre-wetting, this supposes that Pb-17Li was directly adherent on to the steel surface.  
• \textit{De facto}, there is no indication about the polishing treatment, and the presence of a superficial oxide cannot be excluded.  
[Sample, 2000] |

| F82H-mod | 400             | 15 mm gauge length 3 mm diameter Normalised at 1040°C (30 min) Tempered at 750°C (1 h) | Pre-wetting achieved by heating specimens in Pb-17Li at 500°C for 15 h in argon-filled glove box Prior tensile test in Pb-17Li (semi-industrial production, described in [Coen, 1984]) | 1.1 \times 10^{-4} | \( \sigma_{0.2} = 546 \text{ MPa} \) \( \sigma_{TS} = 546 \text{ MPa} \) \( \text{A(\%) = 14.7} \) | • No embrittling effect of Pb-17Li on F82H-mod and OPTIFER IVb in present testing conditions: tensile behaviour unaffected with respect to air reference and (fully dimpled) fracture surface.  
• Assuming complete pre-wetting, this supposes that Pb-17Li was directly adherent on to the steel surface.  
• \textit{De facto}, there is no indication about the polishing treatment, and the presence of a superficial oxide cannot be excluded.  
[Sample, 2000] |

| F82H-mod | 250             | 15 mm gauge length 3 mm diameter Normalised at 950°C (30 min) Tempered at 730°C (3 h) | Pre-wetting achieved by heating specimens in Pb-17Li at 500°C for 15 h in argon-filled glove box Prior tensile test in Pb-17Li | 1.1 \times 10^{-4} | \( \sigma_{0.2} = 488 \text{ MPa} \) \( \sigma_{TS} = 488 \text{ MPa} \) \( \text{A(\%) = 15} \) | • No embrittling effect of Pb-17Li on F82H-mod and OPTIFER IVb in present testing conditions: tensile behaviour unaffected with respect to air reference and (fully dimpled) fracture surface.  
• Assuming complete pre-wetting, this supposes that Pb-17Li was directly adherent on to the steel surface.  
• \textit{De facto}, there is no indication about the polishing treatment, and the presence of a superficial oxide cannot be excluded.  
[Sample, 2000] |

| OPTIFER IVb | 250 | For reference specimens tested in vacuum: additional heat treatment at 500°C for 15 h in vacuum | 1.1 \times 10^{-4} | \( \sigma_{0.2} = 569 \text{ MPa} \) \( \sigma_{TS} = 569 \text{ MPa} \) \( \text{A(\%) = 16.6} \) | | • However, when one simulates an HAZ (heat-affected zone) with these materials, an embrittling effect is seen at 250°C whereas the ductility is recovered at 400°C in otherwise identical conditions.  
• \textit{A(\%) = plastic strain at rupture.} |

| OPTIFER IVb | 400 | 15 mm gauge length 3 mm diameter Normalised at 950°C (30 min) Tempered at 730°C (3 h) | Pre-wetting achieved by heating specimens in Pb-17Li at 500°C for 15 h in argon-filled glove box Prior tensile test in Pb-17Li | 1.1 \times 10^{-4} | \( \sigma_{0.2} = 540 \text{ MPa} \) \( \sigma_{TS} = 540 \text{ MPa} \) \( \text{A(\%) = 17.1} \) | • However, when one simulates an HAZ (heat-affected zone) with these materials, an embrittling effect is seen at 250°C whereas the ductility is recovered at 400°C in otherwise identical conditions.  
• \textit{A(\%) = plastic strain at rupture.} |

| OPTIFER IVb | 250 | 15 mm gauge length 3 mm diameter Normalised at 950°C (30 min) Tempered at 730°C (3 h) | Pre-wetting achieved by heating specimens in Pb-17Li at 500°C for 15 h in argon-filled glove box Prior tensile test in Pb-17Li | 1.1 \times 10^{-4} | \( \sigma_{0.2} = 497 \text{ MPa} \) \( \sigma_{TS} = 497 \text{ MPa} \) \( \text{A(\%) = 18.2} \) | • However, when one simulates an HAZ (heat-affected zone) with these materials, an embrittling effect is seen at 250°C whereas the ductility is recovered at 400°C in otherwise identical conditions.  
• \textit{A(\%) = plastic strain at rupture.} |
Table 7.4.8. Embrittlement of martensitic steels in contact with other liquid metals or alloys: lithium and lead-lithium (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{test}}$ ($^\circ$C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Strain rate ($s^{-1}$)</th>
<th>Mechanical data</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>EUROFER 97</td>
<td>480</td>
<td>Not reported</td>
<td>Reference</td>
<td>$3 \times 10^{-3}$</td>
<td>$\sigma_{0.2} = 425$ MPa</td>
<td>• Un-corroded reference.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 mm/min</td>
<td>$\sigma_{TS} = 480$ MPa</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\varepsilon(%) = 80$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Corrosive attack in “semi-stagnant” Pb-17Li.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$(10^{-2}$ m/s) at $480^\circ$C in LIFUS loop: 40 mm/year.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>The samples extracted from the test section of the loop after 1500 h being covered by Pb-17Li, the authors assumed that wetting occurred during this period of exposure.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Benamati, 2002]</td>
</tr>
<tr>
<td>EUROFER 97</td>
<td>480</td>
<td>Not reported</td>
<td>1500 hours in LIFUS II loop* at $480^\circ$C Prior tensile test under argon (without cleaning the specimens)</td>
<td>$3 \times 10^{-3}$</td>
<td>$\sigma_{0.2} = 415$ MPa</td>
<td>• The tensile behaviour of EUROFER 97 is unaffected by long-term exposure to Pb-17Li in LIFUS II loop, in spite of the corrosive attack.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\sigma_{TS} = 460$ MPa</td>
<td>• This behaviour contrasts markedly with that of T91 after long-term exposure to Pb-55Bi in LECOR loop, in which case the fracture surface after 1500 or even 4500 h of corrosion exhibits a mixed fracture surface (brittle at the periphery, ductile at the centre).</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\varepsilon(%) = 80$</td>
<td></td>
</tr>
<tr>
<td>EUROFER 97</td>
<td>480</td>
<td>Not reported</td>
<td>3000 hours in LIFUS II loop at $480^\circ$C Prior tensile test under argon (without cleaning the specimens)</td>
<td>$3 \times 10^{-3}$</td>
<td>$\sigma_{0.2} = 400$ MPa</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\sigma_{TS} = 440$ MPa</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\varepsilon(%) = 80$</td>
<td></td>
</tr>
<tr>
<td>EUROFER 97</td>
<td>480</td>
<td>Not reported</td>
<td>4500 hours in LIFUS II loop at $480^\circ$C Prior tensile test under argon</td>
<td>$3 \times 10^{-3}$</td>
<td>$\sigma_{0.2} = 400$ MPa</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\sigma_{TS} = 446$ MPa</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\varepsilon(%) = 80$</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>$T_{\text{test}}$ (°C)</td>
<td>Specimen preparation and heat treatment</td>
<td>Environmental testing conditions</td>
<td>Strain rate, traverse rate</td>
<td>Mechanical data</td>
<td>Remarks</td>
</tr>
<tr>
<td>--------------------------</td>
<td>------------------------</td>
<td>----------------------------------------------------------------------------------------------------------</td>
<td>---------------------------------</td>
<td>---------------------------</td>
<td>-----------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
</tbody>
</table>
| Armco iron (0.37%C)      | 200 to 600             | Cylindrical smooth specimen of 9 mm diameter; Annealed at 1100°C (2 h); Grain size: 35 μm                | Exposure to molten Cd, Ga, Bi, Pb, Sn, LBE and Bi-Cd eutectic, Gauge portion of specimens pre-tinned using the method of soldering fluxes | 5%/min         | –                | • Efficient wetting obtained by pre-tinning, “even by such media as liquid lead and bismuth” sic  
• Adsorption-induced facilitation of plastic flow leads to strain-hardening, and takes place in an earlier deformation stage in contact with LM than in vacuum, which promotes localisation of the plastic deformation and a change in the rupture mechanism, and may result in LME effects.  
• Elongation to rupture reduced for Cd, Bi, Pb, Sn, Pb-Bi and Bi-Cd Eutectics, between 225 and 425°C.  
• Interpretation of results based on Rebinder effect.  
• Maximum effect of environment at ~350°C.  
• Complete recovery of plasticity at 450-500°C.  
• No effect of Ga on tensile behaviour, tentatively explained by the formation of solid solutions and intermetallics, which prevents the formation of cracks in regions of pronounced plastic deformation.  
• This is not a general rule, after the authors. | [Popovich, 1978] |
|                          |                        |                                                                                                          | Tensile test in LM under vacuum (10^{-5} Pa of residual pressure) in the 200-600°C range |                   |                  |                                                                                                           |                               |
| Specimens coated with Ga, Pb, Bi, and LBE (as above) Tested in air | 5%/min | – | • Unsuccessful tests: specimens de-wetted due to interfacial oxidation caused by atmospheric oxygen diffusing throughout the metal films. | [Popovich, 1978] |
| Specimens coated with Sn and Cd (as above) Tested in air             | 5%/min | – | • The plasticity of the specimens coated with tin and cadmium were found identical in air and vacuum. |                               |
### Table 7.4.10. Brief survey of the Russian literature (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{test}$ (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Mechanical testing conditions</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>20Kh13 steel</td>
<td>450</td>
<td>Hardened state see Ref. 44 in [Popovich, 1979]</td>
<td>Vacuum</td>
<td>Fatigue testing</td>
<td>• Long-term fatigue strength of 20Kh13 steel reduced in contact with Pb-Sn eutectic. • Stress cannot exceed 80 kgf/mm².</td>
</tr>
<tr>
<td>Carbon steel</td>
<td></td>
<td>Specimens annealed to produce a pearlitio-ferritic structure [7.5 cm diameter “Class 9” surface finish]</td>
<td>Air</td>
<td>Fatigue testing in rotation bending at stress-reversal frequency of 25, 80 and 160 cps</td>
<td>• Fatigue strength of smooth carbon steel specimens in liquid tin and tin-lead eutectic is higher than in air at same temperature, with no effect of stress reversal frequency. • Endurance in Pb-Sn eutectic at 250°C much higher than in air; same for tin at 400°C, with an effect of frequency on notched specimens.</td>
</tr>
<tr>
<td>Steel St. 45</td>
<td>25; 250; 400</td>
<td>Smooth specimens V-shape circular groove 0.5 mm deep Occluded notch angle: 50° Notch root radius: 0.03 mm</td>
<td>Pb-Sn eutectic at 250°C</td>
<td></td>
<td>Hypothesis: Superficial intermetallics (FeSn$_2$….) give rise to high compressive stresses that increase the steel endurance.</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td></td>
<td>Tin at 400°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steel-20</td>
<td>400</td>
<td>40 mm gauge length and 10 mm diameter Used as delivered</td>
<td>Air reference</td>
<td>10 mm/min</td>
<td>Embrittlement of the steel at “high” deformation rate (10 mm/min), in contact with the melts. Plasticity recovered at “slow” deformation rate (0.055 mm/min).</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pre-tinned specimen tested in Pb-Sn eutectic</td>
<td>0.055 mm/min</td>
<td>Hypothesis: Plasticising effect of surface active melt for a certain combination of temperature and deformation rate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pre-tinned specimen tested in LBE</td>
<td>10 mm/min</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Cr18Ni9Ti steel</td>
<td>500</td>
<td>–</td>
<td>Un-tinned specimens fatigue tested in stagnant/flowing LBE at 500°C</td>
<td>Fatigue testing conditions not reported</td>
<td>Pre-tinning with LBE (coated with LBE) using the more suitable soldering flux, prior testing. Sharp reduction in fatigue strength of pre-tinned specimens at 500°C, by comparison with un-tinned specimens, tested either in stagnant &amp; flowing LBE, or in air.</td>
</tr>
<tr>
<td>1Cr18Ni9Ti steel</td>
<td>500</td>
<td>–</td>
<td>Specimens pre-tinned with LBE, then fatigue tested in LBE at 500°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Cr18Ni9Ti steel</td>
<td>600</td>
<td>–</td>
<td>Specimens pre-tinned with LBE, then fatigue tested in air at 600°C</td>
<td></td>
<td>Reduction of the oxygen partial pressure leads to the formation of a protective, stable FeCr$_2$O$_4$ oxide onto the steel surface at 600°C, which explains the steel strength and its endurance limit by inhibiting the potential damage due to LBE. FeCr$_2$O$_4$ films are not destroyed by flowing LBE. Otherwise, in case of formation of brittle oxides, reduction in fatigue strength of both tinned and un-tinned specimens occurs, due to LBE at 600°C in the low endurance range (up to 2 10$^7$ cycles).</td>
</tr>
<tr>
<td>1Cr18Ni9Ti steel</td>
<td>600</td>
<td>–</td>
<td>Specimens pre-tinned with LBE, then tested under pure argon at 600°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Cr18Ni9Ti steel</td>
<td>600</td>
<td>–</td>
<td>Specimens pre-tinned with LBE, then tested in stagnant or flowing LBE at 600°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Cr18Ni9Ti steel</td>
<td>600</td>
<td>–</td>
<td>Un-tinned specimens tested in LBE at 600°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>T (°C)</td>
<td>Specimen preparation and heat treatment</td>
<td>Environmental testing conditions</td>
<td>Mechanical testing conditions and results</td>
<td>Remarks</td>
</tr>
<tr>
<td>-----------------------</td>
<td>--------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>12KhM pearlitic steel</td>
<td>200 to 600</td>
<td>Cylindrical specimens of 20 mm gauge length and 4 mm diameter Prepared from forged 15 mm diameter rods Normalised at 990°C and tempered at 710°C Surface preparation: cleaning in benzene, polishing with emery paper, cleaning in benzene</td>
<td>Specimen pre-tinned with LBE using the method of soldering fluxes (containing zinc chloride and 7% ammonia chloride) Then held 30 min at the test temperature in ampoule filled with LBE (LM surface in contact with air)</td>
<td>Tensile test (uniaxial tension) at 6.25%/min</td>
<td>Influence of LBE on mechanical behaviour maximised on pre-tinned specimens. Maximum reduction of ductility at 400°C independently of the surface preparation (mechanical polishing or pre-tinning). No corrosion by LBE.</td>
</tr>
<tr>
<td>12KhM pearlitic steel</td>
<td>500</td>
<td>As above Pre-tinned with LBE + 0.5 h exposure to LBE under air at 500°C Prior testing in LBE at 500°C</td>
<td>6.25%/min</td>
<td>( \sigma_{0.2} = 35 \text{ kg/mm}^2 ), ( \sigma_{YS} = 48.7 \text{ kg/mm}^2 ), A(%) = 12%</td>
<td>No effect of holding time in oxygen-saturated LBE, from 0.5 h to 25 hours, on the tensile behaviour of 12KhM steel at same temperature. <strong>Hypothesis:</strong> Formation of an interfacial oxide film, which hinders wetting and prevents any embrittling effect.</td>
</tr>
<tr>
<td>12KhM pearlitic steel</td>
<td>500</td>
<td>As above Pre-tinned with LBE + 2.5 h exposure to LBE under air at 500°C Prior testing in LBE at 500°C</td>
<td>6.25%/min</td>
<td>( \sigma_{0.2} = 33.6 \text{ kg/mm}^2 ), ( \sigma_{YS} = 43.8 \text{ kg/mm}^2 ), A(%) = 25.2%</td>
<td>No effect of holding time in oxygen-saturated LBE, from 0.5 h to 25 hours, on the tensile behaviour of 12KhM steel at same temperature. <strong>Hypothesis:</strong> Formation of an interfacial oxide film, which hinders wetting and prevents any embrittling effect.</td>
</tr>
<tr>
<td>12KhM pearlitic steel</td>
<td>500</td>
<td>Pre-tinned with LBE + 5.0 h exposure to LBE under air at 500°C Prior testing in LBE at 500°C</td>
<td>6.25%/min</td>
<td>( \sigma_{0.2} = 34 \text{ kg/mm}^2 ), ( \sigma_{YS} = 45.3 \text{ kg/mm}^2 ), A(%) = 21.6%</td>
<td>No effect of holding time in oxygen-saturated LBE, from 0.5 h to 25 hours, on the tensile behaviour of 12KhM steel at same temperature. <strong>Hypothesis:</strong> Formation of an interfacial oxide film, which hinders wetting and prevents any embrittling effect.</td>
</tr>
<tr>
<td>12KhM pearlitic steel</td>
<td>500</td>
<td>Pre-tinned with LBE + 10 h exposure to LBE under air at 500°C Prior testing in LBE at 500°C</td>
<td>6.25%/min</td>
<td>( \sigma_{0.2} = 33.4 \text{ kg/mm}^2 ), ( \sigma_{YS} = 43.9 \text{ kg/mm}^2 ), A(%) = 21.9%</td>
<td>No effect of holding time in oxygen-saturated LBE, from 0.5 h to 25 hours, on the tensile behaviour of 12KhM steel at same temperature. <strong>Hypothesis:</strong> Formation of an interfacial oxide film, which hinders wetting and prevents any embrittling effect.</td>
</tr>
<tr>
<td>12KhM pearlitic steel</td>
<td>500</td>
<td>Pre-tinned with LBE + 25 h exposure to LBE under air at 500°C Prior testing in LBE at 500°C</td>
<td>6.25%/min</td>
<td>( \sigma_{0.2} = 32.5 \text{ kg/mm}^2 ), ( \sigma_{YS} = 43.3 \text{ kg/mm}^2 ), A(%) = 21.7%</td>
<td>No effect of holding time in oxygen-saturated LBE, from 0.5 h to 25 hours, on the tensile behaviour of 12KhM steel at same temperature. <strong>Hypothesis:</strong> Formation of an interfacial oxide film, which hinders wetting and prevents any embrittling effect.</td>
</tr>
</tbody>
</table>
Table 7.4.10. Brief survey of the Russian literature (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Mechanical testing conditions and results</th>
<th>Remarks</th>
</tr>
</thead>
</table>
| 12KhM pearlitic   | 500    | Cylindrical specimens of 20 mm gauge length and 4 mm diameter Pre-tinning with LBE + 5.0 h exposure to LBE under air Tested after cleaning and re-tinning with LBE | Pre-tinning with LBE + 5.0 h exposure to LBE under air Tested after cleaning and re-tinning with LBE | 6.25%/min σ_{0.2} = 34.1 kg/mm² σ_{YS} = 43.9 kg/mm² A(%) = 11% | • Pre-tinning is considered as “a unique procedure” allowing for the establishment of an intimate contact between steel and LBE, since the steel will always be oxidised in oxygen-saturated LBE and neither Pb nor Bi wet oxides of steel constituents.  
• Re-tinning with LBE after exposure to oxygen-saturated LBE for durations going from 2.5 h to 25 restores the embrittling effect of LBE.  
• drawback of pre-tinning: due to the well-known detrimental effect of zinc, which was tested and found negligible by the authors of this work.  
• However, with increasing tensile strain, cracks can form in the surface oxide and permit contact with the steel surface. In such case, the embrittling effect of the LM would be just delayed (an argument already considered in SCC).  
• Pre-tinning remains the best way to force the steel/LM contact, provided there is no loss of this contact due to a growing oxide at the SM/SL interface, for example caused by inward penetration of oxygen species throughout the metal layers …  
• Postulat: The ductility of steels could be reduced at temperatures > 500°C if no formation of an oxide film takes place on the surface of specimens already wetted by LBE. | [Balandin, 1970] |
| steel             | 500    | Prepared from forged 15 mm diameter rods Normalised at 990°C and tempered at 710°C Surface preparation: cleaning in benzene, polishing with emery paper, cleaning in benzene Pre-tinning with LBE + 25 h exposure to LBE under air Tested after cleaning and re-tinning with LBE | Pre-tinning with LBE + 25 h exposure to LBE under air Tested after cleaning and re-tinning with LBE | 6.25%/min σ_{0.2} = 33.8 kg/mm² σ_{YS} = 43.7 kg/mm² A(%) = 10.8% | | [Balandin, 1970] |
Table 7.4.10. Brief survey of the Russian literature (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Mechanical testing conditions and results</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>St 50 steel</td>
<td>400</td>
<td>Hollow cylindrical specimens (D/d = 16/10) provided with screwed-on jacket</td>
<td>Hollow and ext. jacket filled with LBE Pre-tinning before testing in LBE</td>
<td>Strain rates: 0.05%/min 31.8%/min Cyclic deformation in torsion</td>
<td>Efficient wetting obtained by pre-tinning. Strain-hardening during the first two cycles followed by continuous decrease in strength until fracture at 31.8%/min strain rate. Plasticising effect of LBE is suggested at slow strain rate (0.05%/min.).</td>
<td>[Chaevskii, 1969]</td>
</tr>
<tr>
<td>04X16H11M3T austenitic steel</td>
<td>350</td>
<td>Cylindrical specimens of 5 mm diameter</td>
<td>Air reference</td>
<td>$\sigma_{0.2} = 158 \text{ MPa}$ $\sigma_{YS} = 474 \text{ MPa}$ $\Lambda(%) = 42.7$ $\text{RAZ(%) = 72.5}$ $\sigma_{\text{fracture}} = 1789$</td>
<td>No effect of Pb-17Li on 04X16H11M3T in present testing conditions: tensile behaviour of specimens pre-tinned with Pb-17Li unaffected with respect to air reference (cf. [Chopra, 1986]).</td>
<td>[Antipenkov, 1991]</td>
</tr>
<tr>
<td>04X16H11M3T austenitic steel</td>
<td>350</td>
<td>Cylindrical specimens of 5 mm diameter</td>
<td>Specimens cleaned with zinc chloride Pre-tinned with Pb-17Li Prior tensile testing</td>
<td>$\sigma_{0.2} = 241 \text{ MPa}$ $\sigma_{YS} = 471 \text{ MPa}$ $\Lambda(%) = 49.3$ $\text{RAZ(%) = 66.3}$ $\sigma_{\text{fracture}} = 1193$</td>
<td>No embrittling effect of lead on the 08Kh16N11S3MB austenitic steel in the considered temperatures range and deformation rates. Slight influence of lead, tending to decrease very slightly the strength and ductility of pre-tinned austenitic steel in the 300-450°C range. Plasticising effect of the lead melt in the 400-500°C range. No effect of lead at T &gt; 500°C.</td>
<td>[Abramov, 1994]</td>
</tr>
<tr>
<td>08Kh16N11S3MB austenitic chromium-nickel steel</td>
<td>300 to 700</td>
<td>Flat specimen of 10 mm length and 1 $\times$ 3 mm working cross-section Austenitised at 1050°C (0.5 h)</td>
<td>Reference specimen (without coating) Tensile tested under same conditions</td>
<td>$8 \times 10^{-4} \text{s}^{-1}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 7.4.10. Brief survey of the Russian literature (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Strain rate</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kh12MVSFBR ferritic/martensitic steel</td>
<td>300 to 700</td>
<td>Flat specimen of 10 mm length and 1 x 3 mm working cross-section</td>
<td>Reference specimen Tensile tested under same conditions</td>
<td>8. $10^{-4}$ s$^{-1}$</td>
<td>Strength of reference and tinned specimens decreases with increasing test temperature, whereas the plasticity increases with $T_{test}$. Liquid Pb hardens the Kh12MVSFBR martensitic steel when heat-treated in mode TT-1. Effect of Pb increases at $T \geq 400°C$ (TT-1 case). Plasticity of specimens in contact with molten lead is lower than that of original specimens in the 300-500°C range: – maximum decrease of plasticity at 450°C: $K_p = \delta_p/\delta = 0.5$ with $\delta_p$ and $\delta$ being respectively the specific elongation of the pre-tinned and reference specimens; – plasticity recovered at $T \geq 600°C$.</td>
</tr>
<tr>
<td>Kh12MVSFBR ferritic/martensitic steel</td>
<td>300 to 700</td>
<td>Flat specimen of 10 mm length and 1 x 3 mm working cross-section</td>
<td>Pre-tinning under argon coating by a thin Pb layer (at 350°C) Followed by tensile testing</td>
<td>8. $10^{-4}$ s$^{-1}$</td>
<td>TT-2 heat treatment yields to a noticeable decrease in the plasticity of tinned specimens and to a broadening of the ductility trough, going from 350 to 600°C. Maximum decrease of plasticity at 450°C: $K_p = \delta_p/\delta = 0.2$. Plasticity recovered at 700°C. For pre-tinned specimens: (at an embrittling temperature) well visible cracks, filled with Lead, propagate, at least initially, in the direction normal to the loading axis. Crack propagation is spasmodic (see [Soldatchenkova, 1972]). LME effects are typical of Cr steels, and become more pronounced in the hardened martensite phase. LME effects can be moderated by tempering at high temperature and formation of $\delta$ ferrite.</td>
</tr>
<tr>
<td>Kh12MVSFBR ferritic/martensitic steel</td>
<td>300 to 700</td>
<td>Flat specimen of 10 mm length and 1 x 3 mm working cross-section</td>
<td>Pre-tinning under argon coating by a thin Pb layer (at 350°C) Followed by tensile testing</td>
<td>8. $10^{-4}$ s$^{-1}$</td>
<td>Heat treatment TT-2 leads to a significant increase in strength: $\sigma_{0.2} \geq 1100$ MPa at 300°C.</td>
</tr>
</tbody>
</table>

[Abramov, 1994]
Table 7.4.10. Brief survey of the Russian literature (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Strain rate</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armco iron (0.037 wt.% C)</td>
<td></td>
<td>Cylindrical specimen of 9 mm diameter Stress concentrators with 0.75 mm depth notched with a polishing wheel (60° angle and 0.1 mm curvature radius) Annealing &amp; grain size: 500°C (1 h) → 26 µm 1100°C (2 h) → 80 µm 1250°C (5 h) → 110 µm</td>
<td>Under vacuum (1.3 x 10^-3 Pa)</td>
<td>8.3 x 10^-3 s^-1</td>
<td>• From 100 to 350°C, σTS of smooth specimens increases due to Dynamic Strain Ageing (DSA).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pre-tinning with Pb-Bi followed by tensile testing in Pb-Bi under vacuum</td>
<td></td>
<td>8.3 x 10^-3 s^-1</td>
<td>• Significant LME effect on specimens with stress concentrators: considerable decrease in strength for T ≥ 250°C in both LMs (In, LBE).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pre-tinning with indium followed by tensile testing in indium under vacuum</td>
<td></td>
<td>8.3 x 10^-4 s^-1</td>
<td>• Decrease in strength (σTS) begins at temperatures &lt; Tm of indium, whereas, for LBE, no embrittling effect is observed below 200°C, i.e. well above Tm of LBE.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• Suggestion: Tendency to LME is a consequence of strained state and testing conditions, the temperature of the melt being only one factor among the others.</td>
</tr>
<tr>
<td>Armco iron (0.037 wt.% C)</td>
<td></td>
<td>Square cross-section of 6 x 6 mm (obtained by polishing the lateral surfaces of the cylindrical specimens) Annealed at 1100°C (2 h) Average grain size ~ 80 µm</td>
<td>Under vacuum</td>
<td>8.3 x 10^-4 s^-1</td>
<td>• For specimens with square cross-sections (where faces play the role of stress concentrators), the tensile behaviour is intermediate between the one obtained with “plain” specimens and the other one obtained on specimens with stress concentrators.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pre-tinning with indium followed by tensile testing in indium under vacuum</td>
<td></td>
<td>8.3 x 10^-4 s^-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• 2nd conclusion: Specimens tested with stress concentrators reveal that the higher the level of embrittlement, the lower the temperature of its initiation; this result is consistent with modelling taking into account the influence of the adsorbing medium on plastic deformation in surface layers [Dmukhovs’ka, 1982].</td>
</tr>
</tbody>
</table>

Table 7.4.10. Brief survey of the Russian literature (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Mechanical testing conditions and results</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armco iron</td>
<td>700 to 1000</td>
<td>Hollow cylindrical specimens of 9 mm external diameter and 4 mm internal diameter</td>
<td>Indium (self fluxing medium at HT)</td>
<td>Tensile test at $8.3 \times 10^{-4}$ s$^{-1}$ -</td>
<td>-</td>
</tr>
</tbody>
</table>
|                      |        |                                        |                                  |                                          | • Indium embrittles Armco iron in the 850-950°C temperature range.  
• LME is caused by an indium-induced decrease in flow stress, which localises strain in the α phase and initiates its premature cracking.  
• Indium corrodes Armco iron.  
• Fracture surface of embrittled specimens is microscopically flat.  
• It is proved that corrosion is not responsible for high temperature LME. |
|                      |        |                                        |                                  |                                          | Dmukhov’s’ka, 1993, b |
|                      | 400    | No coating                             | Air reference                    | $\sigma_{0.2} = 265$ MPa  
$\sigma_{fs} = 480$ MPa  
A(%) = 23  
RA(%) = 63 | -                                                                                                                                                          |
|                      | 400    | Ni coating                             | Air environment                  | $\sigma_{0.2} = -$  
$\sigma_{fs} = 500$ MPa  
A(%) = -  
RA(%) = 63 | -                                                                                                                                                          |
| 1Cr-1.5Si-0.5Mo steel | 400    | Without coating                        | Un-wetted surface tested in Pb-Bi | $\sigma_{0.2} = \sigma_{fs} = 500$ MPa  
A(%) = 46  
RA(%) = 46 | -                                                                                                                                                          |
|                      | 400    | Surface wetted by soldering            | Tested in Pb-Bi                  | $\sigma_{0.2} = \sigma_{fs} = 451$ MPa  
A(%) = 20  
RA(%) = 38 | -                                                                                                                                                          |
|                      | 400    | Ni coating                             | Tested in Pb-Bi                  | $\sigma_{0.2} = 274$ MPa  
$\sigma_{fs} = 480$ MPa  
A(%) = 13  
RA(%) = 16 | -                                                                                                                                                          |
|                      | 400    | Surface oxidation                      | Prior testing in Pb-Bi           | $\sigma_{0.2} = 225$ MPa  
$\sigma_{fs} = 451$ MPa  
A(%) = 23  
RA(%) = 58 | -                                                                                                                                                          |

[352] [Gorynin, 1999]
Table 7.4.11. Chemical compositions of the above mentioned steels (wt.%, balance Fe)

| Steel     | Cr  | W   | Ni  | Mn  | V   | Nb  | Mo  | Ta  | Ti  | Al  | Cu  | As  | Sn  | C   | N   | P   | S   | B   | Si  | Ref.         |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----------------|
| T91       | 8.26| 0.13| 0.38| 0.2 | 0.08| 0.95|     |     | 0.024| 0.08| 0.02| 0.008| 0.105| 0.055| 0.009| 0.003| 0.43| [*]|
| MANET     | 10.37| –  | 0.657| 0.76| 0.21| 0.16| 0.5B| –   | –   | 0.007| 0.01| –   | –   | 0.10| 0.032| 0.004| 0.005| 0.0075| 0.18| [Glasbrenner, 2003]|
| 1.4914    | 10.6 | 0.82| 0.54| 0.24| 0.19| 0.49|     |     | 0.05 | 0.01|     |     |     | 0.172|     | 0.005| 0.005| 0.002| 0.34| [Borgstedt, 1986]|
| HT9       | 11.8 | 0.52| 0.51| 0.50| 0.33| –   | 1.03| –   | –   | –   | –   | –   | –   | 0.21| –   | –   | –   | –   | 0.21| [Chopra, 1986]|
| F82H-mod  | 7.66| 2.0 | 0.16| 0.16| –   | 0.02|     |     |     |     |     |     |     | 0.09| 0.005|     |     |     |     | 0.11| [Sample, 2000]|
| OPTFER IVb| 8.3 | 1.4 | 0.34| 0.22| –   | 0.06|     |     |     |     |     |     |     | 0.12| 0.03 |     |     |     |     |     | [Sample, 2000]|
| EUROFER 97| 8.8 | 1.15| 0.44| 0.2 | 0.002| 0.003|     |     |     |     |     |     |     | 0.10| –   |     |     |     |     | 0.05| [Benamati, 2002]|
| 04X16H11M3T| 15.79| 0.1 | 0.6 | 1.3 | –   | 2.18| 0.32| –   | –   |     |     |     |     | 0.04| –   | 0.012| 0.015| –   | 0.54| [Antipenkov, 1991]|

Table 7.5.1. Fatigue behaviour of martensitic and austenitic steels in heavy liquid metals

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{test}}$ (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Mechanical testing conditions</th>
<th>Results and Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MANET</td>
<td>550</td>
<td>Heat treatment: 900-940°C (2 h) 1075°C (30 min) then 750°C (2 h)</td>
<td>Under argon</td>
<td>Strain control: Strain amplitude range from 0.006 to 0.0125</td>
<td>LCF tests in Pb-17Li gives a longer fatigue life than in gaseous environment.</td>
<td>[Borgstedt, 1991]</td>
</tr>
<tr>
<td>MANET</td>
<td>550</td>
<td>Hourglass shape specimen: 8.8 mm min. diameter 21 mm gauge length</td>
<td>Stagnant Pb-17Li (provided by Metallgesellschaft A.G., Frankfurt)</td>
<td>1000 h pre-exposure to Pb-17Li</td>
<td>Prolonged preliminary contact with Pb-17Li reduces this beneficial effect.</td>
<td></td>
</tr>
<tr>
<td>*316L</td>
<td>450</td>
<td>Under argon with 5-10 ppm O$_2$ and 10-15 vL.ppm H$_2$O</td>
<td>Strain control: Average strain = 0.05 superimposed to strain cycle $0.008 \leq \Delta \varepsilon \leq 0.016$ $5 \times 10^{-5} \leq \dot{\varepsilon} \leq 1.07 \times 10^{-4}$ Cycle frequency: 0.0033 Hz Non-fully-reversed triangular wave form</td>
<td>Under argon: Numerous finger-like cracks, some of which propagate deeply in 316L.</td>
<td>Transgranular crack propagation.</td>
<td></td>
</tr>
<tr>
<td>*316L</td>
<td>450</td>
<td>Hourglass shape specimen: 10 mm gauge length Surface finish: total roughness of 1.5 to 2 μm</td>
<td>30 hours pre-exposure to Pb-17Li to wet the specimen Prior LCF test at a flow velocity of 0.01 m/s in the LIFUS II loop</td>
<td></td>
<td>Tensile strain limit slightly higher than compressive strain limit in order to enhance the corrosive effect on crack tip generated by fatigue.</td>
<td>ASTM E606 standard.</td>
</tr>
</tbody>
</table>

*354

<table>
<thead>
<tr>
<th>Material</th>
<th>(T_{\text{test}}) (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Mechanical testing conditions</th>
<th>Results and remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 316</td>
<td>593</td>
<td>For specimen preparation, see Refs. [25-32] of O.K. Chopra, J. Nuclear Mat., 115, 223 (1983).</td>
<td>Pre-exposure (for 1500 h….) to sodium of controlled purity (0.4 ppm carbon) Between 550 and 700°C or thermal ageing for long duration</td>
<td>For mechanical testing conditions, see Refs. [25-32] of O.K. Chopra, J.N.M., 115, 223 (1983)</td>
<td>Fatigue behaviour in sodium superior to that in air, environmental effects being negligible in low oxygen containing sodium (≤ 3 ppm), with a steel surface considered absolutely free from corrosion products.</td>
</tr>
<tr>
<td>316LN</td>
<td>540</td>
<td>Cut from a 40 mm thick plate in the as-received state (solution annealed) with the rolling direction parallel to the chevron-notch (T-L orientation) 12.5 mm thick compact tensile specimen</td>
<td>Designed chamber to allow for continuous flow of LM around CT specimen. Flowing sodium continuously purified: ≤ 2 ppm oxygen; carbon and nitrogen activities also controlled</td>
<td>Under load control (ASTM E-647) using a sine wave form at 5 Hz To simulate service type loading: (R = 0.6, 0.8)</td>
<td>Fatigue crack growth rate in sodium and argon at 540°C considerably lower than in oxidising air environment at same temperature.</td>
</tr>
<tr>
<td>316LN</td>
<td>540</td>
<td></td>
<td></td>
<td></td>
<td>Strong R-dependence of (\Delta K_{\text{th}}) in air and sodium: (\Delta K_{\text{th}}) decreasing with increasing R: from 6 MPa(\text{vm}) for (R = 0.6) to .4 MPa(\text{vm}) for (R = 0.8); same for air or argon cover gas.</td>
</tr>
<tr>
<td>316LN</td>
<td>Room T</td>
<td>Uniform gauge fatigue specimen machined parallel to the primary rolling direction of the 25 mm thick plate used 12.7 mm gauge length 5.08 mm diameter Polishing conditions missing</td>
<td>Air</td>
<td>R = -1</td>
<td>Fatigue endurance limit, in air, decreases from 240 MPa at (R = -1), to 170 MPa for (R = 0.1).</td>
</tr>
<tr>
<td>316LN</td>
<td>Room T</td>
<td></td>
<td>Air</td>
<td>(R = 0.1) (tensile mean stress) Cycle frequency: 0.1, 1, 10 Hz</td>
<td>Fatigue life reduced in Hg compared to air, the effect being amplified with decreasing cycle frequency from 10 Hz to 0.1 Hz. This effect nearly disappears at high frequency (700 Hz, (R = 0.1), temperature control for CF in air).</td>
</tr>
<tr>
<td>316LN</td>
<td>Room T</td>
<td></td>
<td>Hg</td>
<td>(R = -1) Cycle frequency: 0.2 to 0.5 Hz</td>
<td>Wetting and LME: From the observation that Hg is adherent onto the fracture surface and not on the gauge length, it is conjectured that Hg plays a role on crack propagation, by accelerating the crack propagation rate, but not at the stage of crack initiation.</td>
</tr>
<tr>
<td>316LN</td>
<td>Room T</td>
<td></td>
<td>Hg</td>
<td>(R = 0.1) (tensile mean stress) Cycle frequency: 0.1, 1.0, 10 Hz</td>
<td></td>
</tr>
</tbody>
</table>

[Chopra, 1983] [Mishra, 1997] [Strizak, 2001]
Table 7.5.1. Fatigue behaviour of martensitic and austenitic steels in heavy liquid metals (cont.)

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{test}}$ (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Mechanical testing conditions</th>
<th>Results and remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>Room T</td>
<td>Cylindrical specimen: fabricated using “low stress grinding and polishing” treatment 40 mm gauge length 10 mm diameter Tested in as-received state</td>
<td>Air</td>
<td>Total strain amplitude control: 0.3% $\leq \epsilon_{a} \leq 1%$ $R = -1$, triangular waveform Frequency: 1 Hz for all tests</td>
<td>Fatigue life of 316L rather comparable in air and LBE at low strain amplitude (0.3%), even for $\Delta e$ attaining 1%. Cyclic softening: For 316L and MANET II independent of environment, air or LBE, under present experimental conditions. Crack propagation: Slightly faster in LBE than in air for 316L, under present conditions ($\Delta e = 0.3%$, 1 Hz, 260°C).</td>
<td>[Kalkhof, 2003]</td>
</tr>
<tr>
<td>MANET II</td>
<td>260</td>
<td>Cylindrical specimen: fabricated using “low stress grinding and polishing” treatment 40 mm gauge length 10 mm diameter Tested in as-received state</td>
<td>Stagnant LBE</td>
<td>Total strain amplitude control: 0.3% $\leq \epsilon_{a} \leq 1%$ $R = -1$, triangular waveform Cycle frequency: 0.1 Hz</td>
<td>Fatigue life: longer for 316L than for MANET II. Fatigue life of MANET II clearly reduced in LBE: – reduced of $\sim 2$, for $\Delta e = 0.3%$ at 1 Hz; – reduced of $\sim 7$, for $\Delta e = 0.3%$ at 0.1 Hz; (Reduction amplified with decreasing cycle frequency.) – with a large scatter in the number of cycles for crack initiation. Cyclic softening: for MANET II, independent of environment, air or LBE. Hypothesis: LBE affects surf., not bulk properties. Crack propagation: very fast in LBE compared to air for MANET II, in present conditions ($\Delta e = 0.3%$, 1 Hz, 260°C); it is suggested that wetting of crack walls results in an additional tensile stress during crack closure, hindering crack tip blunting. Main hypothesis: wetting of crack walls by LBE!</td>
<td>[Kalkhof, 2003]</td>
</tr>
<tr>
<td>T91</td>
<td>300</td>
<td>Cylindrical specimen: 10 mm gauge length 10 mm diameter Electropolished Austenitised: 1050°C (1 h) Tempered: 750°C (1 h)</td>
<td>Stagnant LBE under air</td>
<td>Total strain range control: 0.36% $\leq \epsilon_{a} \leq 2.4%$ $R = -1$, symmetrical triangular waveform Constant strain rate: $\dot{\epsilon} = 4 \times 10^{-3} \text{s}^{-1}$ 0.08 Hz $\leq$ frequency $\leq 0.55$ Hz</td>
<td>Fatigue life of T91 reduced in LBE, compared to air: – reduced of $\sim 2$, for $\Delta e = 2.2%$ at 0.33 Hz. Fatigue crack initiation: low density of short cracks in LBE, compared to air. Fatigue crack propagation: very fast in LBE, compared to air.</td>
<td>[Vogt, 2004, 2006], [Verleene, 2006]</td>
</tr>
</tbody>
</table>
Table 7.5.2. Fatigue and creep fatigue behaviour of austenitic and martensitic steels in lead alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{test}}$ (°C)</th>
<th>Specimen preparation and heat treatment</th>
<th>Environmental testing conditions</th>
<th>Mechanical testing conditions</th>
<th>Results and remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91</td>
<td>300</td>
<td>Cylindrical specimen: 10 mm gauge length 10 mm diameter Electro-polished Austenitised at 1050°C (1 h) tempered at 750°C (1 h)</td>
<td>Air</td>
<td>Symmetrical triangular wave form ($R = -1$)</td>
<td>• Stress response to strain cycling for all tests, unmodified by hold time, in air or in LBE</td>
<td>[Vogt, 2006]</td>
</tr>
<tr>
<td>T91</td>
<td>300</td>
<td></td>
<td>Air</td>
<td>Trapezoidal wave form (10 min. hold time in tension) Two tests with $\Delta e = 2.5$, 1.6%</td>
<td>• Fatigue life: – reduced for T91 in LBE by introduction of 10 min hold time for $0.4% \leq \Delta e \leq 2.5%$; – unmodified in air in similar conditions.</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>300</td>
<td></td>
<td>Stagnant LBE (no OCS)</td>
<td>Symmetrical triangular wave form ($R = -1$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>300</td>
<td></td>
<td>Stagnant LBE (no OCS)</td>
<td>Trapezoidal wave form 10 min hold time in tension</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>300</td>
<td>Four-point bent specimens: 10 mm x 10 mm x 55 mm</td>
<td>Air</td>
<td>Specific device, using pre-cracked specimens Load ratio $R = 0.5$ Cycle frequency: 5 Hz</td>
<td>• Fatigue crack growth: faster in LBE than in air; in agreement with the results of Kalkhof &amp; Grosse (2003).</td>
<td>[Vogt, 2006]</td>
</tr>
<tr>
<td>0.4Kh16N11M3T</td>
<td>357</td>
<td>Specimens made by stamping sheet materials; then polished over the surfaces and along the contour Working part: 15 mm in length &amp; 1.5 x 5 mm cross-section Blanks austenitised at 1050°C (1 h)</td>
<td>Specimens covered with Pb-17Li melt in a pressure chamber prior fatigue testing in Pb-17Li under cover gas</td>
<td>Symmetric pure bending, total strain amplitude ≤ 3% Low-cycle tests: cycle frequency: 0.5 Hz High-cycle test: cycle frequency: 8.3 Hz</td>
<td>• Fatigue life of austenitic 0.4Kh16N11M3T and 03Kh20N45M4BCh alloys reduced by contact with Pb-17Li under low-cycle loading at 250 and 350°C. • This effect increases with increasing $\Delta e$. • The amplitude of total deformation, $\Delta e$ (in %), at the fatigue limit, is decreased due to contact with Pb-17Li (base: 10^7 cycles).</td>
<td>[Dmukhovs'ka, 1995]</td>
</tr>
</tbody>
</table>
Table 7.5.3. Chemical compositions of the above mentioned steels (wt.%, balance Fe)

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>W</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>V</th>
<th>Nb</th>
<th>Ta</th>
<th>Al</th>
<th>Ti</th>
<th>Cu</th>
<th>Co</th>
<th>As</th>
<th>Sn</th>
<th>C</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>B</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MANET</td>
<td>10.6</td>
<td>0.87</td>
<td>0.77</td>
<td>0.82</td>
<td>0.37</td>
<td>0.22</td>
<td>0.16</td>
<td>0.054</td>
<td>0.015</td>
<td>0.01</td>
<td>0.13</td>
<td>0.020</td>
<td>0.005</td>
<td>0.04</td>
<td>0.0085</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Borgstedt, 1991]</td>
<td></td>
</tr>
<tr>
<td>316L</td>
<td>17.34</td>
<td>12.5</td>
<td>2.40</td>
<td>0.32</td>
<td>0.042</td>
<td>0.042</td>
<td>0.008</td>
<td>0.12</td>
<td>0.03</td>
<td>0.02</td>
<td>0.08</td>
<td>0.02</td>
<td>0.0006</td>
<td>0.0014</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Chopra, 1983]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>316LN</td>
<td>10.50</td>
<td>0.644</td>
<td>0.55</td>
<td>0.927</td>
<td>0.263</td>
<td>0.001</td>
<td>0.006</td>
<td>0.08</td>
<td>0.007</td>
<td>0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Mishra, 1997]</td>
</tr>
<tr>
<td>MANET II</td>
<td>17.2</td>
<td>12.6</td>
<td>2.60</td>
<td>1.67</td>
<td>0.370</td>
<td>0.003</td>
<td>0.35</td>
<td>0.02</td>
<td>0.024</td>
<td>0.003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Kalkhof, 2003]</td>
</tr>
<tr>
<td>316L</td>
<td>8.8</td>
<td>1.07</td>
<td>1.00</td>
<td>0.38</td>
<td>0.41</td>
<td>0.25</td>
<td>0.07</td>
<td>0.003</td>
<td>0.35</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Strizak, 2001]</td>
</tr>
<tr>
<td>T91b</td>
<td>8.5</td>
<td>1.02</td>
<td>1.05</td>
<td>0.47</td>
<td>0.22</td>
<td>0.21</td>
<td>0.06</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Vogt, 2004]</td>
</tr>
<tr>
<td>T91c</td>
<td>15.8</td>
<td>11.7</td>
<td>2.4</td>
<td>1.5</td>
<td>0.54</td>
<td>0.03</td>
<td>0.34</td>
<td>0.2</td>
<td>0.04</td>
<td>0.008</td>
<td>0.008</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316LNa</td>
<td>16.31</td>
<td>10.2</td>
<td>2.07</td>
<td>1.75</td>
<td>0.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MANET II</td>
<td>10.50</td>
<td>0.644</td>
<td>0.55</td>
<td>0.927</td>
<td>0.263</td>
<td>0.001</td>
<td>0.006</td>
<td>0.08</td>
<td>0.007</td>
<td>0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Kalkhof, 2003]</td>
</tr>
<tr>
<td>316L</td>
<td>17.2</td>
<td>12.6</td>
<td>2.60</td>
<td>1.67</td>
<td>0.370</td>
<td>0.003</td>
<td>0.35</td>
<td>0.02</td>
<td>0.024</td>
<td>0.003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Strizak, 2001]</td>
</tr>
<tr>
<td>T91b</td>
<td>8.8</td>
<td>1.07</td>
<td>1.00</td>
<td>0.38</td>
<td>0.41</td>
<td>0.25</td>
<td>0.07</td>
<td>0.003</td>
<td>0.35</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Vogt, 2004]</td>
</tr>
<tr>
<td>T91c</td>
<td>8.5</td>
<td>1.02</td>
<td>1.05</td>
<td>0.47</td>
<td>0.22</td>
<td>0.21</td>
<td>0.06</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Vogt, 2004]</td>
<td></td>
</tr>
<tr>
<td>04Kh16N11M3T</td>
<td>15.8</td>
<td>11.7</td>
<td>2.4</td>
<td>1.5</td>
<td>0.54</td>
<td>0.03</td>
<td>0.34</td>
<td>0.2</td>
<td>0.04</td>
<td>0.008</td>
<td>0.008</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Dmukhovs’ka, 1995]</td>
</tr>
<tr>
<td>03Kh20N45M4BCh</td>
<td>19.0</td>
<td>45.6</td>
<td>3.8</td>
<td>0.6</td>
<td>0.26</td>
<td>0.75</td>
<td>0.85</td>
<td>0.12</td>
<td>0.003</td>
<td>0.08</td>
<td>0.18</td>
<td>0.01</td>
<td>0.0004</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[Dmukhovs’ka, 1995]</td>
<td></td>
</tr>
</tbody>
</table>

a 316LN supplied by Jessop Steel Company, heat 18474 type 316 LN.
b T91 supplied by Creusot-Loire Industrie.
c T91 supplied by Ascometal.
Chapter 8
IRRADIATION EFFECTS ON COMPATIBILITY OF STRUCTURAL MATERIALS WITH LEAD-BISMUTH EUTECTIC (LBE)*

8.1 Introduction

The interaction between several materials in the presence of static or flowing lead alloys was performed in a number of laboratories at different temperatures, flow rates, oxygen contents, surface and heat treatment conditions. In the past few years many results concerning corrosion attack and possibilities to prohibit it were generated in the 5th FP (TECLA) [JNM, 2004] and some investigations are still ongoing in the 6th FP (DEMETRA) [Fazio, 2005]. The examinations are in the early stage concerning mechanical tests in the presence of lead or lead alloy and may have an influence on mechanical properties. As of this date there are no other sources of data available and the chapter can only focuses on a very few sets of data. Of great interest is to understand the mechanism of liquid metal embrittlement (LME) and to identify the cause of damage. In Chapters 6 and 7 of this handbook the compatibility of structural materials with LBE and mechanical properties in LBE are covered. In Chapter 9 the knowledge is summarised on lead and LBE corrosion protection existing up to now.

Another important issue is the material behaviour during irradiation. The change of material properties because of irradiated with protons and/or neutrons has to be fully understood. The effects of irradiation on mechanical properties generally manifest themselves on one hand as an increase in the yield stress (radiation hardening) and on the other hand as a decrease in ductility (radiation embrittlement) [Jung, 2002].

The main objective therefore is to determine whether irradiation will promote embrittlement and corrosion attack by liquid metal. The investigations are just in the early stage and only a limited number of experiments have been launched in this field up to now.

In the experimental facility LiSoR at PSI the specimens are placed directly in the LBE flow while irradiated with protons/neutrons. The experimental conditions for operating the loop and the irradiation beam parameters are presented and the results of analysis of the irradiated specimens (surface and cross-section) and of the tensile tests are discussed in Section 8.2. Pre-oxidised martensitic ferritic steel HT9 has been irradiated with protons at the LANSCE WNR facility in Los Alamos, USA, in the presence of LBE. The results are discussed in Section 8.2 as well.

SCK•CEN has irradiated the steels AISI 316L, T91, EM10 and HT9 in the BR2 reactor in Mol, Belgium. After irradiation, tensile tests were performed in the presence of LBE. The experimental conditions and the results are presented in Section 8.3.

At PSI several different materials (in contact with Pb and LBE) have been irradiated in the SINQ facility with protons/neutrons. Mechanical tests are foreseen to be performed in LBE. Some details concerning the test programmes including the irradiation conditions are described in Section 8.4.

* Chapter lead: Heike Glasbrenner (PSI, Switzerland). For additional contributors, please see the List of Contributors at the end of this work.
In Section 8.5 a brief overview on the irradiation experiments planned to be performed within the DEMETRA (6th FP) is given.

8.2 Irradiation of ferritic-martensitic steel T91 with protons and neutrons in LBE (PSI)

The DIN 1.4903 steel 9Cr1MoVNb named T91 was supplied by the company CLI-FAFER (France) and has a composition in wt.% of 8.41 Cr, 0.08 Ni, 0.95 Mo, 0.44 Mn, 0.31 Si, 0.1 C, 0.25 V, 0.08 Nb, 0.24 Si, 0.035 Cu, 0.002 S with Fe in balance. The material was delivered in standard heat treated conditions, i.e. the steel was normalised at 1070°C for 1 h followed by air cooling, and then tempered at 765°C for 1 h followed by air cooling.

8.2.1 LiSoR

LiSoR (Liquid-metal/Solid-metal Reaction) is a unique facility to investigate simultaneously the influence of flowing LBE, static mechanical stress and additional fluctuating thermal stress under irradiation of a steel probe. LiSoR facility is actually a LBE loop installed at a proton beam line of Injector-I at PSI. The energy of the proton beam is 72 MeV. Protons with this energy can penetrate about 10 cm in steels or LBE [Kirchner, 2003].

8.2.2 Irradiation

For performing the post-irradiation experiments (PIE) the samples of interest are the test-section tube (TS-tube) and inner tensile-stressed specimen (TS-specimen) in the test section. Both the wall of the TS-tube and the TS-specimen are 1 mm in thickness. Figure 8.2.1 describes the geometry of the specimen. In Figure 8.2.2 the sketches show the test tube made of T91 and the cross-section including the specimen and the flowing LBE.

During irradiation (including beam-off time) a constant mechanical load was applied upon the tensile specimen and the temperature of inlet LBE was constantly controlled at 300°C. In the TS-tube and TS-specimen the irradiation areas are about 5.5 × 14 mm². In the irradiation areas the proton beam induced localised temperature increase and thermal stress oscillated with the wobbled proton beam at a frequency of about 2 Hz. The materials and irradiation parameters are listed in Table 8.2.1 for the four irradiation campaigns, LiSoR-2 to LiSoR-5. The details of the experiments and the temperature and stress distributions are given in [Glasbrenner, 2005a], [Kirchner, 2003], [Samec, 2005]. As an example Figure 8.2.3 shows the calculated temperature, stresses in longitudinal/transversal directions and shear stress changing with time at a point in the irradiation area of the TS-specimen LiSoR-5 [Samec, 2005].

Figure 8.2.1. Nominal dimensions of the specimen irradiated in test section no. 2 to 5
Figure 8.2.2. Sketches show the test tube and its cross-section including the specimen and flowing LBE.

Table 8.2.1. Materials and irradiation conditions of the TS-tubes and TS-specimens of LiSoR-2 to LiSoR-5

<table>
<thead>
<tr>
<th>Irradiation time</th>
<th>LiSoR-2</th>
<th>LiSoR-3</th>
<th>LiSoR-4</th>
<th>LiSoR-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>TS-tube</td>
<td>TS-tube</td>
<td>TS-tube</td>
<td>TS-tube</td>
</tr>
<tr>
<td></td>
<td>T91-A</td>
<td>T91-B</td>
<td>T91-B</td>
<td>T91-C</td>
</tr>
<tr>
<td></td>
<td>T91-A</td>
<td>T91-B</td>
<td>T91-B</td>
<td>T91-A</td>
</tr>
<tr>
<td>Averaged proton energy</td>
<td>TS-tube</td>
<td>T91-4 MeV</td>
<td>70 MeV</td>
<td>70 MeV</td>
</tr>
<tr>
<td></td>
<td>TS-specimen</td>
<td>40 MeV</td>
<td>40 MeV</td>
<td>40 MeV</td>
</tr>
<tr>
<td>Beam current</td>
<td>TS-tube</td>
<td>50 μA</td>
<td>50 μA</td>
<td>30 μA</td>
</tr>
<tr>
<td></td>
<td>TS-specimen</td>
<td>15 μA</td>
<td>15 μA</td>
<td>15 μA</td>
</tr>
<tr>
<td>Peak oscillating temp. LBE-surf.</td>
<td>TS-tube</td>
<td>650°C</td>
<td>330°C</td>
<td>400°C</td>
</tr>
<tr>
<td></td>
<td>TS-specimen</td>
<td>580°C</td>
<td>324°C</td>
<td>380°C</td>
</tr>
<tr>
<td>Peak oscillating temp. maximum</td>
<td>TS-tube</td>
<td>–</td>
<td>380°C</td>
<td>550°C</td>
</tr>
<tr>
<td></td>
<td>TS-specimen</td>
<td>–</td>
<td>345°C</td>
<td>440°C</td>
</tr>
<tr>
<td>Maximum stress</td>
<td>TS-tube</td>
<td>200 MPa</td>
<td>25 MPa</td>
<td>75 MPa</td>
</tr>
<tr>
<td></td>
<td>TS-specimen</td>
<td>200 MPa</td>
<td>200 MPaC</td>
<td>200 MPa</td>
</tr>
<tr>
<td>Irradiation dose</td>
<td>TS-tube</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>TS-specimen</td>
<td>0.075</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>He concentration</td>
<td>TS-tube</td>
<td>3.6 appm</td>
<td>7.2 appm</td>
<td>7.2 appm</td>
</tr>
<tr>
<td></td>
<td>TS-specimen</td>
<td>2.6 appm</td>
<td>5.2 appm</td>
<td>5.2 appm</td>
</tr>
</tbody>
</table>

1. T91-A, the material of the tube produced by Creusot Loire Industrie (France) and has a composition in wt.% of 8.26 Cr, 0.13 Ni, 0.95 Mo, 0.43 Si, 0.38 Mn, 0.1 C, 0.2 V, 0.017 P, 0.065 Nb and with Fe in balance.
2. T91-B, the material of the TS-specimen: from SPIRE programme supplied by Ugine (France) and has a composition in wt.% of 8.63 Cr, 0.23 Ni, 0.31 Si, 0.43 Mn, 0.1 C, 0.21 V, 0.02 P, 0.09 Nb and with Fe as balance. The material was normalised at 1040°C for 1 h followed by air cooling, and then tempered at 760°C for 1 h followed by air cooling.
3. T91-C, the material of the TS-specimen of LiSoR-5.
4. [Kirchner, 2003] Figure 8.
5. [Samec, 2005].
6. [Samec, 2005]. The maximum temperature in the TS-specimen is in the central position (0.5 mm depth) while for the tube it is at the outer surface.
7. [Samec, 2005]. For the TS-tube it is the maximum shear stress. In fact the TS-tube has a maximum compression stress which is 6 times larger than the shear stress.
8. [Samec, 2005].
9. The helium concentration of LiSoR-2 was measured [Dai, 2006b]. The others were calculated using LiSoR-2 data.
8.2.3 Surface analyses

The surface analyses of LiSoR samples have been performed in different ways: visual inspection (photography), SEM, EPMA and SIMS.

The photos of the visual inspection have been taken from the irradiation areas of both the TS-tubes and the TS-specimens of the four irradiations, as shown in Figure 8.2.4. In the upper photos the beam foot print on each TS-tube can be clearly seen. In the LiSoR-2 TS-tube, a crack was formed due to high temperature and high thermal stress induced by small beam size [Dai, 2004]. No other evident damages were observed in other TS-tubes. The LBE on LiSoR-2 TS-tube was leaking out from the crack. On the surfaces of the TS-specimens one can see some remaining of LBE. On the TS-specimens of LiSoR-2 and -5 a significant amount of adherent LBE is visible, which can be attributed to either higher temperature (LiSoR-2) or longer time of exposure (LiSoR-5) compared to LiSoR-3 and -4. The irradiation areas in LiSoR-2 and -5 specimens are quite easy to recognise, while in those of LiSoR-3 and -4 are more difficult. There are some deposits on the surfaces of LiSoR-2 and -5 specimens below the irradiation areas.

After the visual inspection, the TS-tubes and TS-specimens were cut with an EDM machine into small dog-bone shaped tensile samples for tensile testing, and the remaining pieces between the tensile samples were saved for TEM, SEM, SIMS, etc. analyses.
SEM (for low activity samples) or EPMA (for high activity samples) analyses were carried out to inspect the surface after irradiation in contact with LBE. As of this date samples from LiSoR-2, -3 and -5 have been analysed [Dai, 2004], [Glasbrenner, 2005a, 2005b, 2006].

The general feature is the formation of an oxide scale of up to few microns thickness on the surface in the irradiated areas, as illustrated in Figure 8.2.5. One can see that the oxide layer of LiSoR-2 is the thickest while that of LiSoR-3 is thinnest. From the irradiation conditions given in Table 8.2.1 one can conclude that the variation of the thickness of the oxide scale depends mainly on the irradiation temperature but that the irradiation time plays a role as well. However, this cannot be clarified here since the temperatures in the cases are different. This can be done when LiSoR-4 is inspected, since the temperatures of LiSoR-4 and LiSoR-5 are the same due to the identical irradiation parameters. From the difference between LiSoR-2 and the others, it is clear that the temperature effect is much more pronounced than the time effect.

The inner surface of the LiSoR-2 TS-tubes was not reworked after EDM wire cutting and before irradiation. After the leakage incident of LiSoR-2, the TS-tubes for the following LiSoR irradiations were polished on the inner surfaces to remove the micro-cracked layer. The three micrographs in Figure 8.2.6 show the inner surface of the LiSoR-2 TS-tube, the cross-sections of LiSoR-2 and LiSoR-3 TS-tubes, respectively. It can be seen that the surface after EDM cutting is very rough.
(micrograph a) and cracks of a depth of about 10 μm were introduced in the surface layer (micrograph b). Mechanical polishing removed the damaged layer with microcracks of the inner surface layers of the LiSoR-3 to -5 TS-tubes (micrograph c).

The LBE on the surfaces of the TS-specimens of LiSoR-2 and LiSoR-5 have been analysed. Figure 8.2.5 shows an example of LiSoR-5. The region observed is below the irradiation area where a lot of precipitation adhered on the surface. The element analysis indicates Pb and Bi mostly separated due to re-crystallisation.

An important point should be noted is that, except for the TS-tube of LiSoR-2, no other microcracks were observed either in the TS-specimens or in the TS-tubes, even in the LiSoR-2 TS-specimen where the material of the irradiation area experienced about 120000 cycles of fatigue deformation at a relatively high stress and temperature [Glasbrenner, 2005a].

**Figure 8.2.5. SEM (a and b) and EPMA (c) micrographs showing the cross-sections in the irradiation areas of (a) LiSoR-2, (b) LiSoR-3 and (c) LiSoR-5 TS-specimens**

**Figure 8.2.6. Graphs show (a) the inner surface of LiSoR-2 TS-tube, (b) the cross-sections of LiSoR-2 TS-tube and (c) the cross-sections of LiSoR-3 TS-tube**

**Figure 8.2.7. Wave Dispersive Spectrometers (WDS) analysis of LBE on the surface of the TS-specimen of LiSoR-5**

364
SIMS analyses were carried out on several samples of LiSoR-2 to -5. An element depth profile obtained on a sample from the irradiation area of the TS-specimen of LiSoR-3 is shown in Figure 8.2.8 [Glasbrenner, 2006].

Figure 8.2.8. Fe, Cr, FeO and Pb depth distribution profile measured in the irradiation area in LiSoR-3 TS-specimen

A small amount of $^{208}$Pb was evident in the most outer layers of the sample, whereas the element Bi was not detected. The species $^{52}$FeO and $^{56}$Fe followed the same trend: Their amount stayed constant up to a depth of app. 400 nm, whereas $^{52}$Cr was not detected in this area. With increasing depth a decrease of Fe and FeO took place and in parallel the amount of Cr increased from nearly zero, ran through a maximum and then decreased again. The maximum was in a depth of about 500 nm. The gradients of the Cr, Fe and FeO species achieved on the samples adjacent to the beam centre showed the same trend. In Figure 8.2.9 the Fe and Cr curves of the three samples from the TS-specimen of LiSoR-5 are put together in a graph for comparison. The thickness of the outer layer, constant amount of Fe and FeO without any Cr, is ~300 nm in a distance of 13 mm of the beam centre and ~250 nm in a distance of 24 mm. The peaks of Cr are ~400 nm at 13 mm distance and ~350 nm at 24 mm distance, respectively. It is well known that oxides formed on ferritic-martensitic steels consist of double structured oxides: the outer layer is the Cr-free iron oxide, and the layer beneath is a FeCr$_2$O$_4$ spinel. The present SIMS results agree with the general observations.

Figure 8.2.9. Fe (left) and Cr (right) depth distributions measured at different positions in LiSoR-3 TS-specimen
8.2.4 Tensile tests

As mentioned above, one of the main purposes of LiSoR experiments is to investigate the LBE embrittlement effects on T91 steel under irradiation. All the inner TS-specimens from LiSoR-2 to -5 were not broken during irradiation, although a mechanical loading of 200 MPa was always applied. This is at least a good indication that shows the material can withstand such mechanical load to a radiation damage level of about 0.75 dpa. To analyse the actual degradation of mechanical properties induced by LBE and irradiation, tensile tests were performed. The samples were divided into two groups. The first group included a part of samples from LiSoR-2 TS-specimens and all samples from the TS-tubes and TS-specimens of LiSoR-3 and LiSoR-5. They were tested in Ar (+2%H₂) atmosphere. The results of these tests should represent the original status of the T91 steel after irradiation in LiSoR. The second group included the rest of LiSoR-2 samples and the samples from LiSoR-4 which has almost the same irradiation dose as LiSoR-3. These samples were tested in LBE. These tests were intended to show additional effects from the testing environment in LBE. All the tests were performed at 300°C. The oxygen content in the LBE was less than 1 wppm [Dai, 2006c].

Figure 8.2.10 presents the tensile results of some LiSoR-3 and LiSoR-5 samples tested in Ar. The samples from the irradiation area of the TS-specimens demonstrate slight hardening induced by irradiation as expected (a and c). However, the hardening in the samples from the irradiation area of the TS-tubes is much less (b and d). This is due to the fact that the temperature in the irradiation area of the TS-tubes was higher ≥350°C, where irradiation hardening effects in martensitic steels are not significant. The ductility is only slightly reduced in samples of LiSoR-3, and more strongly in LiSoR-5. It is clear that the strong reduction of the ductility in LiSoR-5 samples is mostly due to the embrittlement of LBE. As can be seen in Figure 8.2.4, some LBE adhered on the surface of the TS-specimen of LiSoR-5. During EDM cutting or testing, the LBE could enter the microcracks on the side surfaces of the samples, which were produced by EDM cutting, and finally induced the embrittlement effect. For LiSoR-3 samples, since very little LBE adhered on the TS-specimen and TS-tube surfaces, the effect was not pronounced. On the other hand, the irradiation should have a synergetic effect. One can see that the embrittlement is more serious at higher doses in each individual case (a to d). Unfortunately, the present results are compromised by the effects the microcracks on the side surfaces, and therefore do not separate the original irradiation and LBE embrittlement effects solely.

Figure 8.2.11 shows the results of tensile tests performed in LBE of some samples from the TS-specimens of LiSoR-2 and LiSoR-4 tested in oxygen saturated LBE. For comparison, the result of one LiSoR-2 sample tested in Ar is also included. The embrittlement effects of LBE are clearly demonstrated by the significant reduction of ductility. For the irradiation effects, the results indicate also a trend that the embrittlement effects are more evident at higher doses.

8.2.5 Proton irradiation of pre-oxidised HT9 in the presence of LBE at the LANSCE WNR facility (Los Alamos)

Lillard, et al. [Lillard, 2004] investigated pre-oxidised HT9 samples with an oxide scale in the order of 3 μm thickness with impedance spectroscopy while immersed in LBE at 200°C and irradiated with protons in the LANSCE WNR facility.

The energy of the particle beam was 800 MeV and the current of the protons was approximately 63 nA. The impedance spectroscopy was performed before irradiation, during (30 min.) and after irradiation. The results achieved on HT9 pre-oxidised samples during different stages of the experiment diverge among each other and a conclusion concerning the corrosion rate cannot be given definitely. Further experiments are needed to understand fully the process and it has to be critically proven if
Figure 8.2.10. Tensile results of some LiSoR-3 and LiSoR-5 samples performed in Ar

Figure 8.2.11. Tensile results of the some samples from the TS-specimens of LiSoR-2 and -4 tested at 300°C in oxygen saturated LBE; the numbers indicate the irradiation doses
impedance spectroscopy is an appropriate method to assess the corrosion rate in real time during irradiation. It is well-known that beside gamma-ray, X-ray, electron and neutron irradiation [Noda, 1995], [Tanifuji, 1998], [Shikama, 1998], [Vila, 2000] as well proton irradiations of insulating oxides [Sato, 2004], [Hunn, 1995] results in transient radiation induced conductivity (RIC) by promoting electrons from the valence band to the conduction band which can also be the reason of the sharp fall in impedance upon turning the beam on. The RIC effect is up to now mostly observed on ceramic materials like Al₂O₃ and MgO but in [Howlader, 1999] the increase of the electrical conductivity proportional to the irradiation flux was observed on Zircaloy oxides. This might happen as well on oxidised steel surfaces which would adulterate the results of the impedance spectroscopy measured during irradiation.

8.3 Irradiation with neutrons in BR2 (SCK•CEN)

The samples were irradiated in BR-2 reactor in Mol and experimental details and the results of these experiments are taken from the paper of [Sapundjiev, 2005]. The irradiation was done in MISTRAL (Multipurpose Irradiation System for Testing of Reactor ALloys) in-pile sections (MIPS).

8.3.1 Material

The materials tested were austenitic steel AISI 316L and the ferritic-martenisitic steels T91, HT9 and EM10. The chemical compositions of the materials are given in Table 8.3.1.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>V</th>
<th>Nb</th>
<th>S</th>
<th>Si</th>
<th>N</th>
<th>C</th>
<th>P</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 316L</td>
<td>16</td>
<td>10.1</td>
<td>2.1</td>
<td>1.58</td>
<td>–</td>
<td>–</td>
<td>0.016</td>
<td>0.51</td>
<td>–</td>
<td>0.022</td>
<td>0.029</td>
<td>–</td>
</tr>
<tr>
<td>T91 (1.4903)</td>
<td>8.3</td>
<td>0.13</td>
<td>0.95</td>
<td>0.4</td>
<td>0.2</td>
<td>0.08</td>
<td>0.4</td>
<td>0.02</td>
<td>0.11</td>
<td>–</td>
<td>&lt;0.01</td>
<td></td>
</tr>
<tr>
<td>EM10</td>
<td>8.97</td>
<td>0.07</td>
<td>1.06</td>
<td>0.49</td>
<td>0.013</td>
<td>&lt;0.002</td>
<td>&lt;0.003</td>
<td>0.46</td>
<td>0.014</td>
<td>0.099</td>
<td>0.013</td>
<td>0.01</td>
</tr>
<tr>
<td>HT9</td>
<td>11.68</td>
<td>0.66</td>
<td>1.06</td>
<td>0.63</td>
<td>0.29</td>
<td>0.03</td>
<td>&lt;0.003</td>
<td>0.45</td>
<td>0.204</td>
<td>0.020</td>
<td>0.47</td>
<td></td>
</tr>
</tbody>
</table>

The materials were received in the following conditions:

- AISI 316 L: was supplied by SIDERO STAAL, Belgium, n.v., heat number 744060 in the shape of bars with diameter 6 mm and length 500 mm from which the specimens were manufactured. The material is solution annealed with some cold work.
- T91: supplied by UGINE, France, heat 36224 normalised at 1040°C for 60 min. and tempered at 760°C for 60 min.
- EM10: supplied by CEA France, normalised at 990°C for 50 min., tempered at 750°C for 60 min.
- HT9: normalised at 1050°C for 30 min., tempered at 700°C for 2 h.

The samples used were sub-size tensile samples with a length of 27 mm, gage length of 12 mm and diameter of 2.4 mm. The irradiation temperature was about 200°C [Jacquet, 2003]. The fast neutron flux and fluence (E > 1 MeV) were obtained by multiplying the experimental equivalent fission flux and fluence by 0.87, i.e. the average ratio of the calculated fast flux to the equivalent fission flux [Willekens, 2004]. The calculated doses are given in Table 8.3.2.
Table 8.3.2. Irradiation doses and specimen designations of AISI 316L, T91, EM10 and HT9

<table>
<thead>
<tr>
<th>Material</th>
<th>Dose/dpa</th>
<th>Material</th>
<th>Dose/dpa</th>
<th>Material</th>
<th>Dose/dpa</th>
<th>Material</th>
<th>Dose/dpa</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91</td>
<td>1.14</td>
<td>AISI 316L</td>
<td>1.46</td>
<td>EM10</td>
<td>2.93</td>
<td>HT9</td>
<td>2.53</td>
</tr>
<tr>
<td>T91</td>
<td>1.15</td>
<td>AISI 316L</td>
<td>1.46</td>
<td>EM10</td>
<td>4.36</td>
<td>HT9</td>
<td>4.36</td>
</tr>
<tr>
<td>T91</td>
<td>1.15</td>
<td>AISI 316L</td>
<td>1.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>1.58</td>
<td>AISI 316L</td>
<td>1.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>1.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>2.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>4.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

8.3.2 Tensile tests

Slow strain rate (SSR) tests were performed in an autoclave in conjunction with a gas conditioning system. All tests in LBE were performed at a strain rate of $5 \times 10^{-6}$ s$^{-1}$ and a temperature of 200°C. After a sample was broken, it was removed from the autoclave and cleaned in hot tempering oil at 160-180°C for about 5 min.

8.3.3 LBE conditioning

Lead bismuth eutectic alloy (44.8% Pb, 55.2% Bi) was supplied by Hetzel Metalle GmbH, Germany, with reported purity: Pb 99.985% minimum and Bi 99.99% minimum.

Two different oxygen conditions of LBE were investigated. Under oxygen free conditions, the liquid metal was constantly purged with 5% H$_2$ in Ar gas mixture during the experiment.

The pre-conditioning in both cases (oxygen “free” and oxygen controlled atmosphere) was achieved by bubbling of 5% H$_2$ in Ar gas mixture or H$_2$/H$_2$O mixture respectively into the liquid LBE for approximately 4 hours.

8.3.4 Effect of irradiation and liquid Pb-Bi eutectic on AISI 316L irradiated to 1.7 dpa

The tensile curves from the SSR tests are plotted on Figure 8.3.1. In the same figure the SSRT curve of non-irradiated AISI 316L specimen is given tested under the same conditions for comparison [Sapundjiev, 2004].

Irradiation of AISI 316L resulted in significant hardening and plastic instability after the yield point. The uniform elongation is nearly zero. The stress-strain curves are the same after irradiation up to 1.72 dpa. Their shape does not depend much on the irradiation dose. Irradiation hardening resulted in an increase of the yield ($\sigma_{02}$) and tensile ($\sigma_{UTS}$) strengths of about 27% and 23%. It seems that the presence of liquid metal had a positive effect on these properties in that $\sigma_{02}$ and $\sigma_{UTS}$ decreased with about 3% and 1.5% respectively when tested in LBE which is in the experimental error. Further experiments are needed to clarify if the effect is real.

Regarding the strain to failure, irradiation resulted in irradiation embrittlement and reduction of total elongation of about 27%. When tested in liquid metal the total elongation increased (irrespective to the irradiation dose) by 11-15%, whereas the reduction in area decreased by about 2-11% at different irradiation doses.
The mechanical parameters of AISI 316L were obtained after the analyses of the stress-strain curves and are presented in Table 8.3.3.

Table 8.3.3. Results of the SSRT tests in liquid Pb-Bi on A 316 L material irradiated to different doses at 200°C and strain rate 5.10^{-6} s^{-1}

<table>
<thead>
<tr>
<th>Dose/dpa</th>
<th>Environment</th>
<th>σ_{0.2}, MPa</th>
<th>ε_{tot}, %</th>
<th>ε_{plast}, %</th>
<th>ε_{unif}, %</th>
<th>σ_{UTS}, MPa</th>
<th>σ_{fracture}, MPa</th>
<th>RA, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Pb-Bi</td>
<td>540.17</td>
<td>24</td>
<td>21</td>
<td>8</td>
<td>559.80</td>
<td>347.96</td>
<td>77±5</td>
</tr>
<tr>
<td>1.46</td>
<td>Air (reference)</td>
<td>683.80</td>
<td>13</td>
<td>11</td>
<td>3</td>
<td>689.14</td>
<td>379.44</td>
<td>63±5</td>
</tr>
<tr>
<td>1.46</td>
<td>Pb-Bi</td>
<td>670.72</td>
<td>14</td>
<td>12</td>
<td>0</td>
<td>682.38</td>
<td>421.83</td>
<td>56±5</td>
</tr>
<tr>
<td>1.57</td>
<td>Pb-Bi+ dissolved oxygen</td>
<td>668.71</td>
<td>15</td>
<td>13</td>
<td>0</td>
<td>685.05</td>
<td>411.96</td>
<td>62±5</td>
</tr>
<tr>
<td>1.72</td>
<td>Pb-Bi</td>
<td>663.52</td>
<td>15</td>
<td>13</td>
<td>5</td>
<td>678.94</td>
<td>427.94</td>
<td>59±5</td>
</tr>
</tbody>
</table>

8.3.5 Effect of irradiation and liquid Pb-Bi eutectic on T91 irradiated up to 4.36 dpa

The stress/strain curves of T91 specimens irradiated up to 1.7 dpa and tested in air and in liquid lead-bismuth eutectic are plotted in Figure 8.3.2. The tensile curve of the non-irradiated sample is also provided for comparison, tested in liquid Pb-Bi under the same conditions.

The stress-strain curves of T91 material irradiated to 2.93 and 4.36 dpa are plotted in Figure 8.3.3. In air the material undergoes significant hardening after irradiation and the yield strength approaches about 850 MPa. The irradiation results in reduction of the strain to failure as well. However, the material still deforms plastically although the ultimate and the yield strengths are almost equal. At these doses, the total elongation depends very little on the irradiation dose and tends to saturation.
The results of the SSRT tests performed at 200°C on the T91 samples irradiated up to 4.36 dpa are given in Table 8.3.4. The reference tests in air were performed on samples irradiated to 1.15 dpa, 2.93 and 4.36 dpa. The yield and the ultimate tensile strengths approach constant value at doses >2.93 dpa and tend to be invariant of the irradiation dose both in air and in liquid metal. In liquid metal these parameters are always smaller by about 9% and 7% respectively.

8.3.6 Effect of irradiation and liquid Pb-Bi eutectic on EM10 irradiated up to 4.36 dpa

The stress-strain curves of EM10 material tested in air and in liquid lead-bismuth eutectic after irradiation to 4.36 dpa are plotted on Figure 8.3.4. The material has very similar irradiation behaviour to T91. The latter however show higher irradiation hardening (65% increase in $\sigma_{02}$ and 35% increase in $\sigma_{UTS}$) compared to 60% and 25% for EM10 material.
Table 8.3.4. Results of the SSRT tests in liquid Pb-Bi on T91 material irradiated to different doses at 200°C and strain rate 5.10^{-6} s^{-1}

<table>
<thead>
<tr>
<th>Dose/dpa</th>
<th>Environment</th>
<th>σ_{0.2}</th>
<th>ε_{int}</th>
<th>ε_{plast}</th>
<th>ε_{unif}</th>
<th>UTS</th>
<th>Fracture</th>
<th>RA, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Pb-Bi</td>
<td>482.31</td>
<td>21</td>
<td>19</td>
<td>6</td>
<td>601.23</td>
<td>324.96</td>
<td>77±6</td>
</tr>
<tr>
<td>1.14</td>
<td>Pb-Bi + dissolved oxygen</td>
<td>710.75</td>
<td>16</td>
<td>14</td>
<td>3</td>
<td>734.25</td>
<td>424.90</td>
<td>68±5</td>
</tr>
<tr>
<td>1.15</td>
<td>Air reference</td>
<td>750.71</td>
<td>16</td>
<td>14</td>
<td>3</td>
<td>772.77</td>
<td>462.66</td>
<td>68±5</td>
</tr>
<tr>
<td>1.58</td>
<td>Pb-Bi</td>
<td>731.00</td>
<td>15</td>
<td>13</td>
<td>3</td>
<td>758.31</td>
<td>465.48</td>
<td>61±5</td>
</tr>
<tr>
<td>1.7</td>
<td>Pb-Bi</td>
<td>731.80</td>
<td>16</td>
<td>13</td>
<td>3</td>
<td>763.50</td>
<td>481.66</td>
<td>63±5</td>
</tr>
<tr>
<td>2.93</td>
<td>Air</td>
<td>835.00</td>
<td>0.14</td>
<td>0.12</td>
<td>0.02</td>
<td>838.58</td>
<td>531.41</td>
<td>79</td>
</tr>
<tr>
<td>4.36</td>
<td>Air</td>
<td>835.28</td>
<td>0.13</td>
<td>0.11</td>
<td>0.03</td>
<td>836.39</td>
<td>554.34</td>
<td>65</td>
</tr>
<tr>
<td>2.93</td>
<td>Pb-Bi</td>
<td>756.90</td>
<td>0.13</td>
<td>0.11</td>
<td>0.02</td>
<td>781.93</td>
<td>522.62</td>
<td>64±9</td>
</tr>
<tr>
<td>4.36</td>
<td>Pb-Bi</td>
<td>763.90</td>
<td>0.13</td>
<td>0.11</td>
<td>0.03</td>
<td>799.77</td>
<td>536.33</td>
<td>57±9</td>
</tr>
</tbody>
</table>

Figure 8.3.4. Strain stress curves of EM10 material tested in liquid Pb-Bi at 200°C and strain rate 5.10^{-6} s^{-1} in Pb-Bi and 3.10^{-4} s^{-1} in air

EM10, 200°C, strain rate 5.10^{-6}, s^{-1}

Nevertheless EM10 material still undergoes uniform deformation after irradiation up to 4.36 dpa in air and in LBE. In the latter environment, the total elongation is smaller than in air, but the differences are too small to be assigned to any liquid metal embrittlement. Even at doses as high as 4.36 dpa, the EM10 material deforms plastically and fractures in a ductile manner. The irradiation induced variations decrease with the dose increase and probably will saturate at higher doses. The environmental effect of liquid lead bismuth is very small if it exists at all. The yield and the tensile strengths are slightly smaller in liquid metal than when tested in air.

The results from the SSRT tests on this material irradiated to 2.93 and 4.36 dpa are given in Table 8.3.5 together with the reference tests at the same doses in air as well as the result from the test on non-irradiated material (at 250°C).
Table 8.3.5. Results from the SSRT tests in liquid Pb-Bi on EM10 material irradiated to different doses at 200°C and strain rate 5.10^-6 s^-1 when tested in Pb-Bi and 3.10^-4 s^-1 for the tests in air

<table>
<thead>
<tr>
<th>Dose/dpa</th>
<th>Environment</th>
<th>( \sigma_{0.2} ), MPa</th>
<th>( \varepsilon_{0.2} ), %</th>
<th>( \varepsilon_{plast} ), %</th>
<th>( \varepsilon_{unif} ), %</th>
<th>( \sigma_{UTS} ), MPa</th>
<th>( \sigma_{fracture} ), MPa</th>
<th>RA, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0*</td>
<td>Air</td>
<td>440.99</td>
<td>35</td>
<td>33</td>
<td>8</td>
<td>576.20</td>
<td>272.82</td>
<td>79-80</td>
</tr>
<tr>
<td>2.93</td>
<td>Air</td>
<td>673.39</td>
<td>17</td>
<td>15</td>
<td>2</td>
<td>692.77</td>
<td>357.30</td>
<td>59</td>
</tr>
<tr>
<td>4.36</td>
<td>Air</td>
<td>708.27</td>
<td>16</td>
<td>14</td>
<td>2</td>
<td>717.58</td>
<td>368.10</td>
<td>76</td>
</tr>
<tr>
<td>2.93</td>
<td>Pb-Bi</td>
<td>643.56</td>
<td>17</td>
<td>15</td>
<td>4</td>
<td>674.25</td>
<td>390.99</td>
<td>74±8</td>
</tr>
<tr>
<td>4.36</td>
<td>Pb-Bi</td>
<td>659.54</td>
<td>15</td>
<td>13</td>
<td>2</td>
<td>672.52</td>
<td>378.34</td>
<td>70±9</td>
</tr>
</tbody>
</table>

* At 250°C.

8.3.7 Effect of irradiation and liquid Pb-Bi eutectic on HT9 irradiated up to 4.36 dpa

The stress-strain curves of HT9 material tested in air and in liquid lead-bismuth eutectic after irradiation to 2.53 and 4.36 dpa are plotted on Figure 8.3.5. Irradiation of this material results in hardening and plastic instability reducing mainly the plastic deformation and breaking with almost no necking. The reduction in area when tested in air is about 33 to 34% at 2.53 and 4.36 dpa respectively. In Pb-Bi the reduction in area is slightly higher (38 and 45% at 2.53 and 4.36 dpa).

Figure 8.3.5. Strain stress curves of HT9 material tested in liquid Pb-Bi at 200°C and strain rate 5.10^-6 s^-1 in Pb-Bi and 3.10^-4 s^-1 in air

The results of the mechanical tests in air and in liquid metal for HT9 material are summarised in Table 8.3.8. The reference test on non-irradiated material was performed in air and at slightly lower temperature (150°C).
Table 8.3.6. Results of the SSRT tests in liquid Pb-Bi on HT9 material irradiated to different doses at 200°C and strain rate 5.10^{-6} s^{-1} when tested in Pb-Bi and 3.10^{-4} s^{-1} for the tests in air

<table>
<thead>
<tr>
<th>Dose/dpa</th>
<th>Environment</th>
<th>$\sigma_{0.2}$ MPa</th>
<th>$\varepsilon_{\text{tot}}$ %</th>
<th>$\varepsilon_{\text{plast}}$ %</th>
<th>$\varepsilon_{\text{unif}}$ %</th>
<th>$\sigma_{\text{UTS}}$ MPa</th>
<th>$\sigma_{\text{fracture}}$ MPa</th>
<th>RA, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0*</td>
<td>Air</td>
<td>559.62</td>
<td>18</td>
<td>17</td>
<td>9</td>
<td>744.73</td>
<td>544.90</td>
<td>61</td>
</tr>
<tr>
<td>2.53</td>
<td>Air</td>
<td>960.30</td>
<td>12</td>
<td>9</td>
<td>4</td>
<td>988.86</td>
<td>819.79</td>
<td>33</td>
</tr>
<tr>
<td>4.36</td>
<td>Air</td>
<td>977.91</td>
<td>14</td>
<td>10</td>
<td>5</td>
<td>1037.52</td>
<td>871.23</td>
<td>34</td>
</tr>
<tr>
<td>2.53</td>
<td>Pb-Bi</td>
<td>896.00</td>
<td>14</td>
<td>10</td>
<td>5</td>
<td>967.01</td>
<td>826.79</td>
<td>38±11</td>
</tr>
<tr>
<td>4.36</td>
<td>Pb-Bi</td>
<td>841.00</td>
<td>14</td>
<td>10</td>
<td>6</td>
<td>965.38</td>
<td>846.74</td>
<td>45±10</td>
</tr>
</tbody>
</table>

* At 150°C.

The yield and the tensile strength of HT9 increased by about 72% and 20% at 2.53 dpa and 75% and 25% at 4.36 dpa respectively. Both properties tend to saturation with the irradiation dose as with the previous materials. The effect of the liquid metal is somehow positive on the strength properties. When tested in Pb-Bi the yield and the tensile strength decreased with 7% and 2% at 2.53 dpa and with 14% and 7% at 4.36 dpa respectively compared to the same conditions in air. The SEM inspection of the fracture face of the different samples revealed no difference of their fractures independent on the testing environment.

8.4 Irradiation with proton and neutron spectrum in SINQ targets at PSI

In the SINQ target irradiation programme (STIP) many samples were irradiated or are being irradiated in presence of LBE and pure Pb as well.

In STIP-II [Dai, 2005] which was performed in 2000 and 2001, about 150 samples of different types such as tensile, bending-fatigue, TEM and stressed capsules from more than 10 kinds of ferritic/martensitic (FM) and austenitic steels were irradiated to doses up to 19 dpa in the temperature range 100 to 400°C. In particular, some TEM discs were coated with different kinds of materials by using several methods. Part of these samples have been retrieved and being analysed. The preliminary results should be available around the end of 2006, and detailed investigations should be completed in 2007.

In STIP-IV which is being conducted in the present SINQ target, a number of T91 and SS 316LN samples are being irradiated in contact with LBE and Pb. The irradiation temperature is up to 500°C and the final irradiation dose should be about 20 dpa when the irradiation completed by the end of 2005. The PIE will be performed in 2008.

8.4.1 Mechanical tests on irradiated specimens in LBE

Some FM steel specimens irradiated in STIP-I [Dai, 2001] have been tested in LBE. Figure 8.4.1 shows results from a three-point bending test on pre-cracked T91 samples in Ar and LBE (oxygen saturated) environments [Dai, 2006a]. As illustrated in Figure 8.4.1, LBE embrittlement effect is very clear. For the sample tested in LBE, the crack propagated suddenly through the whole specimen after three loading-unloading cycles and resulted in a brittle fracture. The corresponding fracture toughness value is about 40 MPa$\cdot$V$\cdot$m, which is significantly lower than that of tested in Ar, 105 MPa$\cdot$V$\cdot$m. Systematic tensile and bending tests on sample irradiated in STIP-I and STIP-II will be conducted in 2005 to 2007.
The higher dose may be one reason for the different results achieved on HT9 and were described in the previous section. But the main difference is that the three-point bending tests were performed on “pre-cracked” samples, while the tensile samples irradiated in Mol were smooth samples. SSRT results [Dai, 2006c] on un-irradiated T91 tensile samples indicate that without surface cracks the LME of LBE is hardly to take place. Up to now the results are very limited and further experiments are needed to compare the results achieved on different mechanical testing procedures.

8.5 Future irradiation programmes (DEMETRA programme)

Experimental programme on neutron irradiation/LBE combined effects foreseen in the European project EUROTRANS

In the frame of the DEMETRA domain of the EUROTRANS project, a work package has been foreseen for the study and compilation of data on the irradiation behaviour of reference structural materials in the specific environment of accelerator-driven systems. Two types of reference structural materials were defined: the stainless steel AISI 316L that will be considered for the vessel components and the martensitic steel T91 (9Cr1MoVNb) envisaged for the spallation target structures and core components. In addition, for components in the high temperature regions of the ADS (i.e. core), the use of Fe-Al based coatings is anticipated.

It is well known that irradiation induces specific effects such as defect production (displacement of atoms, dislocation loops, and voids), phase instability (dissolution, precipitation, segregation), changes in chemical composition induced by spallation or transmutation reactions. These important modifications in the material microstructure induce a degradation of mechanical properties, which will affect the lifetime of different components. Besides the consideration on “pure” irradiation, other important contribution to the lifetime of components comes from the presence of flowing LBE alloy. Corrosion mechanisms and embrittlement phenomena can further limit the performances of structural materials.

The experimental approach foreseen within DEMETRA will consist on testing materials with different available experimental tools, like fission reactors including irradiation in LBE, irradiation under mixed proton/neutron spectrum, helium and implantation tests. The experimental activities aim
at studying the combined effects, like in the case of irradiations in presence of LBE in a neutron field, but also to determine and separate each damaging contribution to enhance comprehension of irradiation phenomena.

To investigate the combined effects induced by the irradiation in presence of liquid LBE alloy and to evaluate the contribution of corrosion mechanisms and irradiation damage on the degradation of mechanical properties of T91 steel and selected coatings two irradiation experiments are foreseen. The irradiations will be conducted in the two irradiation facilities BR2 and HFR respectively. BR2 and HFR are two mixed spectrum fission reactors operated by SCK•CEN, Mol, Belgium and NRG, Petten, Netherlands, respectively.

In Table 8.5.1 the test matrix foreseen for the two reactors are reported. This table shows that the irradiation experiments will be performed on the T91 steel in a temperature range of 300-500°C and in a dpa range of 2-5. In addition, in the high temperature range (450 and 500°C), samples of coated T91 steel will be irradiated.

The preparation of the irradiation rig and the licensing of the experiments are started at the time being of preparing this handbook. The set of results of the post-irradiation experiments will be available by the beginning of 2009.

### Table 8.5.1. Test matrix of the HFR and BR2 experiments

<table>
<thead>
<tr>
<th>Reactor</th>
<th>HFR – NRG</th>
<th>BR-2 – SCK•CEN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irradiation temperature</td>
<td>350°C and 500°C</td>
<td>300°C</td>
</tr>
<tr>
<td>Damage</td>
<td>2 dpa</td>
<td>2 dpa</td>
</tr>
<tr>
<td>Material</td>
<td>T91/coating</td>
<td>T91</td>
</tr>
<tr>
<td>Duration</td>
<td>2 dpa, 1 y or 2 dpa, 0.7 y</td>
<td>1.5 y</td>
</tr>
<tr>
<td>Environment</td>
<td>LBE</td>
<td>LBE and H₂O</td>
</tr>
<tr>
<td>O₂ content</td>
<td>&lt;10E-6</td>
<td>&lt;10E-6 &amp; saturated</td>
</tr>
<tr>
<td>Samples</td>
<td>2<em>8 Tensile 2</em>8 Tensile notched 2<em>8 KLST 2</em>8 pre-stressed 2*8 corrosion/coating</td>
<td>24 SSRT 24 control H₂O 36 water 24 CT 10.3 mm 24 CT water plates, corrosion coating</td>
</tr>
<tr>
<td>PIE performed in LBE</td>
<td>With oxygen-controlled atmosphere</td>
<td>Controlled gas phase and LBE</td>
</tr>
<tr>
<td>Po measurements</td>
<td>Po analyses</td>
<td></td>
</tr>
</tbody>
</table>
 REFERENCES


378
Chapter 9

Pb AND LBE CORROSION PROTECTION AT ELEVATED TEMPERATURES*

9.1 Introduction

Compatibility of material with liquid LBE is a key problem for LBE-cooled systems. Steels are attacked by dissolution of the components in LBE. Dissolution has to be minimised or, even better, entirely prevented for the structural cladding and target materials in contact with LBE. One measure that is widely being used for temperatures in the range up to 500°C is dissolution of oxygen in LBE until the oxygen content reaches a level that allows oxidation of the structural material but not oxidation of the LBE [Gromov, 2004], [Müller, 2000], [Benamati, 2000]. This method is described in Chapters 4 and 6 of this Handbook and will not be considered here. Nevertheless, the protection measures described in this chapter in most of the cases work also at oxygen potentials in the above given range or may be effective also at much lower potentials. In this chapter we are concerned with oxide coatings or alloys that develop slowly growing protective oxide scales by reaction of oxygen with alloyed stable oxide formers in the coating at the surface or into the bulk of the alloy material and are suitable for protection of highly loaded parts like claddings, wrappers and spacers at elevated temperatures above 500 up to 650°C [Müller, 2000], [Asher, 1977], [Deloffre, 2004], [Gorynin, 1999]. Other coatings or alloys that are based on refractory low soluble elements or on nitrides and carbides would require very low oxygen potentials to prevent oxidation of the material [Asher, 1977], [Benamati, 2004], [Seifert, 1961], [Block, 1977]. The following materials and modifications are discussed in this chapter for a successful application in liquid LBE systems.

1) Alloys with Al and Si that form thin stable oxide layers in LBE containing appropriate oxygen concentrations;
2) Coatings consisting of oxides, nitrides, carbides or alloys like FeCrAlY that form protective oxide layers in LBE containing oxygen;
3) Coatings with resistant metals with low solubility in LBE like W, Mo, Nb…;
4) Inhibitors like Zr dissolved in LBE that cause formation of a protective surface layer on the structural material.

The methods described in 1-3 divide into those that need oxygen concentrations in LBE in which oxides develop at the surface of structural material or that are high enough to prevent dissociation of oxide coatings and into those in which the oxygen concentration is low enough to prevent extensive oxidation of the protective compounds like nitrides and carbides and of the inhibitors dissolved in LBE. In case of low oxygen concentrations we have to pay attention to its influence on the low temperature part of the reactor for which additional protection methods are not required in LBE with oxygen. The requirement of self healing of the protective layers has to be considered in any case.

* Chapter lead: Georg Müller (FZK, Germany). For additional contributors, please see the List of Contributors at the end of this work.
The requirements on the properties of the material surface that contacts LBE can be summarised as follows:

- prevention of dissolution attack;
- tolerable oxidation rate during oxide scale formation;
- long-term, high-temperature stability of the system also under temporary abnormal conditions;
- tolerable influence of the coating and surface alloying process on the mechanical properties of the structural material;
- durability under irradiation;
- long-term mechanical stability of the surface coating and alloying layer;
- feasibility on an industrial level;
- self-healing ability of protective layers.

9.2 Methods of surface protection

9.2.1 Alloying of stable oxide formers

It is known from several examinations that Al and Si alloyed into the steel within the appropriate concentration range develop thin, stable and protective oxide scales by diffusion of Al or Si to the surface where they react with the oxygen dissolved in LBE. These scales are an effective barrier against diffusion of cations as well as of anions and prevent, thus, a fast growth of the scale that is often observed with the magnetite and spinel layers on FeCr steels. The slow growth of the oxide scale ensures a long time protection function without extensive steel oxidation. Breach of the scale is minimised and if it happens, self healing will occur by diffusion of the scale forming cations to the defect position which mainly consists of small fissures.

The main advantage of alloying Al or Si just into a thin surface layer is obvious. The thin surface layer will not influence the mechanical properties of the bulk material and the scale will have a good adhesion to the surface. Recently, there are some examinations reported on the suitability of Al alloyed into the surface of ferritic and austenitic steel for their protection against dissolution attack of LBE [Müller, 2000], [Deloffre, 2004]. Si was used up to now only as an addition to the bulk material with which a marked improvement of the corrosion resistance was attained [Gorynin, 1999], [Kurata, 2005], [Lim 2006]. It is alloyed into the steel during the industrial production process. An example is the Russian steel EI 852 containing 2 wt.% Si [Yachmenyor, 1999]. However, in principal, surface layers containing an alloy with Si should work as protective oxide scale formers as well.

The procedures for alloying Al into a steel surface layer reported up to date are:

- Melt alloying by melting of the surface covered with an Al foil or with precipitated Al by pulsed electrons beam of large diameter (GESA process) [Müller, 2005].
- Diffusion alloying that constitutes of three different procedures. The first is hot dipping of the steel into an Al melt with subsequent annealing [Glasbrenner, 1998]. The second heating of the steel covered by an Al foil above the melting point of Al [Heinzel, 2002]. The third is pack cementation [Deloffre 2004].
9.2.1.1 Alloying by the GESA process

GESA is a pulsed electron beam facility that consists of a high voltage generator with a pulse duration control unit, a multipoint explosive emission cathode, a controlling grid and an anode which form a triode [Engelko, 2001]. The kinetic energy of the beam electrons can be varied in the range of $50\pm150$ keV, with a beam power density up to 2 MW/cm$^2$ at the target and pulse duration up to 40 $\mu$s. The important parameters for the melting process, electron energy, power density and pulse duration can be chosen independent of each other. The energy density absorption of the target is up to 80 J/cm$^2$, which is sufficient to melt metallic materials adiabatically up to a depth of 10-50 $\mu$m. The beam diameter is 6-10 cm and this is the area of surface melting by applying one single pulse. Due to the high cooling rate, on the order of $10^7$ K/s, very fine grained or even amorphous structures develop during solidification of the molten surface layer. This is a suitable basis for the formation of protective oxide scales with good adhesion [Müller, 2005], [Engelko, 2001].

Surface alloying of the steel specimens was done by applying the electron pulse to the surface covered with an 18 $\mu$m thick Al foil [Müller, 2005]. During surface melting 20-25% of the aluminium is dissolved in the melt layer, the remainder evaporates. The micrographic cross-section and the Al-concentration profile perpendicular to the surface is shown in Figure 9.2.1. The analysis shows that Al penetrates into the steel within the molten surface layer. Profile A was obtained with an 18 $\mu$m Al-foil by applying just one electron pulse and profile B with a second pulse after attaching a new Al-foil. When an additional pulse is applied to a surface with a B-profile without replacing the Al-foil, profile C is obtained, which is almost constant up to a depth of 15 $\mu$m. The concentration profiles are not typical for a diffusion process, but for a distribution by turbulences in the melt. The obtained structure consists of two phases, which contain different Al concentrations (4-10 wt.%) but have the same Cr content. One phase corresponds to Al dissolved in Fe, $\alpha$-Fe(Al), the other is FeAl [Müller, 2000].

Corrosion experiments with alloyed steels show that 4 wt.% Al is high enough to achieve selective alumina scale formation [Asher, 1977]. For concentrations above 20 wt.%, however, the Al activity gets too high and dissolution attack can occur [Müller, 2002].

In a few cases single areas appear after surface alloying in which with Al concentrations are below 4 wt.% because of incomplete overlapping of alloyed surface regions. In such places the steel
would develop normal magnetite and spinel layers like the unalloyed steel surface because the Al content is too low for selective oxidation and alumina formation on the surface. Those defects have to be avoided by sufficient overlapping of the electron beam areas.

Since, structural parts that are exposed to high temperatures, including fuel cladding wrappers and spacers, have to be protected by the alumina layers at the surface, a new GESA IV facility has been constructed which allows surface alloying of tubes with small diameters by employing a cylindrical cathode [Weisenburger, 2005]. A tube length of 32 cm is alloyed with one single pulse on the whole tube and circumferential overlapping on the surface is avoided.

9.2.1.2 Diffusion alloying processes

As opposed to the GESA process the diffusion alloying processes create Al alloys by interdiffusion between the steel matrix and the Al at the surface which is in most cases in a liquid state. The time for interdiffusion should be long enough to lower the Al activity to a value for which no rapid dissolution in LBE takes place. We refer here to three processes: hot dipping, pack cementation and liquefying of an Al foil at the surface.

In the hot dipping process austenitic steel specimens are dipped into liquid Al contained in an alumina crucible under an Ar5%H2 atmosphere [Glasbrenner, 1998]. The temperature of the Al is 700°C and the dipping time around 30 sec. Annealing follows at 500°C for 2 h and finally air cooling to room temperature. The Al layer is typically 50 µm thick with an interdiffusion zone of <10 µm thickness (Figure 9.2.2, left). This is expected to lead to dissolution reactions with the LBE because of the high Al activity at the surface.

Figure 9.2.2. Austenitic 1.4970 steel (left) and martensitic MANET steel (right) after hot dipping at 700°C in Al and subsequent annealing, at 500°C for 2 h and 1050°C for 0.5 h, respectively [Heinzel, 2002]

For martensitic steel (Figure 9.2.2, right), the hot dipping procedure leads to very thick surface layers of Al with >100 µm interdiffusion zones, because of the rapid diffusion of Al into the steel matrix [Glasbrenner 1998]. Thus, hot dipping followed by annealing not a suitable protection method for this type of steel.

For Al-alloying the steel with a liquefied foil a 99% pure Al foil is wrapped around a fresh ground tube and fixed by an Al-spray [Heinzel, 2002]. After a drying time of 12 h at 180°C a heat treatment follows at 1050°C for 0.5 h. A typical cross-section of an Al alloy layer obtained by wrapping the tube sample and annealing is shown in Figure 9.2.3.
Figure 9.2.3. SEM micrograph of the surface cross-section and Al concentration profile of the austenitic 1.4970 steel after melting an Al foil at the surface and subsequent diffusion annealing [Heinzel, 2002]

On top of the original surface there is a FeAl layer which forms by diffusion of iron into the liquid Al layer during annealing. The diffusion zone of 25 µm depth below the surface contains Al dissolved in Fe and NiAl precipitations (dark), while the interface of some µm thickness contains a zone of NiAl created by Ni diffusion. The Al content could be controlled by the thickness of the Al foil, but a simple component geometry is a precondition for this procedure. It is not suitable for martensitic steels because of the high temperature during the heat treatment and the high Al diffusion coefficient in these steels.

Another method to precipitate Al at the steel surface is by pack cementation [Deloffre, 2004] which is industrially available for austenitic steels [ASTM B875-96 (2003)]. In this process, the components to be coated are immersed in a powder mixture containing Al (source), a halide salt (activator) like NaF or similar compounds and an inert diluent such as alumina. When the mixture is heated above 700°C the Al source reacts with the activator to a gaseous compound which carries Al to the substrate. The gas decomposes at the substrate surface depositing Al and releasing the halogen activator or ammonium, respectively. The activator returns to the powder mixture and reacts again with the Al source. A period of several hours is needed to produce such a coating. Afterwards the Al is alloyed into the steel by a heat treatment at 900°C for 6 h under an argon atmosphere. Using austenitic steels such a treatment leads to a 60-70 µm thick alloyed surface layer containing Al, Fe, Cr, Ni and O [Deloffre, 2004]. The layer is divided by precipitates rich in Ni and Al and is similar structured like the layer obtained with a liquefied foil (comp. Figure 9.2.3) with a NiAl rich zone at the interface. Peaks for Ni and Al in the concentration profile of Figure 9.2.4 indicate positions at which the scanning beam meets a NiAl precipitation in the bulk material. In comparison with the surface near region the deeper region, in the bulk material, has a lower Al but a higher Cr concentration.

Pack cementation of martensitic T91 steel by 3 different procedures including alumina deposition at the coated surface did not lead to suitable results for application above 500°C [Deloffre, 2003].

As compared to the GESA surface alloying, the diffusion alloying processes results in a concentration distribution that corresponds to an exponential profile below the original steel surface and to a surface layer which is created by iron diffusion into the liquid Al. GESA alloyed surface layers have an relatively even Al distribution in the whole melt region of about 20 µm. The GESA process can be applied to any steel whilst the diffusion processes are only suitable for austenitic steels because of the rapid Al diffusion in martensitic steels. The hot dipped steels have thick Al layers
which also after annealing have a high Al activity that leads to dissolution attack in LBE [Glasbrenner, 1998]. Alloying by a liquefied Al foil has, compared to hot-dipping, the advantage that the thickness of the Al layer can be controlled by the thickness of the foil [Heinzel, 2002].

9.2.2 Corrosion-resistant coatings

Instead of surface alloying resistant metals, alloys or compounds can be precipitated on the steel surface [Ballinger, 2004]. Resistant metals like W, Mo, Nb or alloys of these metals require a clean environment with very low oxygen activity to prevent oxidation. The metals themselves have a low solubility and are stable in LBE at lower oxygen activities. Alloys like the superalloy MCrAlY [Nicholls, 2003] gain protective behaviour by forming a stable, dense oxide scale on the surface. These alloys require an oxygen activity that causes oxide scale formation and that keeps the scales stable and allows their self-healing. Coatings consisting of resistant compounds like oxides, carbides or nitrides will generally not possess self-healing properties. They must have long time stability and good adhesion to the steel surface which is not easily being achieved.

9.2.2.1 FeCrAlY coatings

MCrAIY coatings (M=Fe, Ni, Co or NiCo) are widely applied for first and second stage turbine blades as corrosion resistant overlays or as bond-coats for use with thermal barrier coatings [Nicholls, 2003]. The corrosion resistance is based on the ability to form alumina layers due to selective oxidation. The coating could be applied by a number of processes like physical vapour deposition (PVD), air plasma spraying (APS) or vacuum plasma spraying (VPS), but the most common is the low pressure plasma spraying (LPPS). Figure 9.2.5 left side shows a cross-section of a cladding tube with a ~20 µm LPPS FeCrAlY coating. Coatings with Co could not be used because of the activation in a reactor and those with Ni not because of the high solubility of Ni in Pb and PbBi.

The coating has a rough surface because of the relatively large spray droplets, contains pores and also the adhesion on the bulk material is not perfect. To exclude these uncertainties, the coatings can be treated using the GESA melting process. Experiments with GESA show that a GESA treatment

---

Footnote:

1 Coating by Sulzer, Wohlen, Switzerland.
smoothes the surface and removes pores. Another important effect of the GESA treatment is that because of the small layer thickness the coating is “welded” to the bulk material. Figure 9.2.5 right side shows such a GESA treated sample [Weisenburger, 2005].

**Figure 9.2.5. FeCrAlY coating on austenitic steel [Weisenburger, 2005]**

*Left: coating after LPPS, right: after GESA electron melt treatment*

Looking at the structure of the GESA treated FeCrAlY (24.8% Cr, 8.7 Al, 0.49% Y, Fe balance) coating on the right side of Figure 9.2.5, it could be argued that the coating attained properties like a surface alloyed layer and could be classified as such a type of surface protection. This is because the melting zone reaches beyond the coating substrate interface and, thus causes a mixing of both materials.

Bulk FeCrAlY (15%Cr, 4% Al, 0.64%Y, 0.015%C, Fe balance) has been examined by Asher, *et al.* [Asher, 1977] in flowing Pb at 700°C and did not show any visible attack also after 13000 h of exposure at low oxygen potential. The same behaviour is observed with FeCrAlY coatings after GESA treatment after first experiments up to 5000 h at 500-600°C [Weisenburger, 2005].

### 9.2.2.2 Coatings with resistant metals

Early experiments on the compatibility of Bi with Ta, Mo and Be were carried out to explore suitable materials for the containment for liquid Bi in a liquid metal fuel reactor [Seifert, 1961]. Up to this time several experiments are reported in which no appreciable attack of Bi at temperatures of up to 1000°C was observed after several 100 h. Bi containing 5%U at 800-1000°C had an average corrosion rate of only 0.025 mm after 5000 h. Later, such experiments were conducted also with LBE [Romano, 1963]. The results are more or less expected if one looks at the low solubilities of these metals in Bi and LBE. Low solubilities are observed also with W and Nb. These metals are all candidates for a coating to protect structural steels against the attack of LBE [Benamati, 2004].

Several coatings with the above mentioned metals were produced by plasma spraying [Block, 1977]. However, only the Mo coating was successful because Mo was the only metal with which a satisfying coating could be achieved. This is because of the high access of oxygen to the plasma beam in which MoO3 evaporates and is not precipitated on the target. There are other possibilities to coat the surface of metals without oxide formation such as employing PVD and CVD processes and electrochemical deposition [Asher, 1977]. However, cracks and spalling occurs with the coatings during temperature changes. An exception was Mo on Croloy. More development work is necessary to explore the potential of such coatings.
It is obvious that dense coatings with metals of low solubility offer a good protection against LBE especially if the oxygen potential of the LBE is below that of the metal oxide formation. If this is not the case, stable oxide layer formation on the metal surface is necessary for an effective protection.

9.2.2.3 Oxide, carbide and nitride coatings

Oxide, carbide and nitride coatings are widely used in industrial applications and the technique of their precipitation on metal surfaces is well developed, e.g. for the hot sections of gas turbines for numerous cases of corrosion protection and wear resistance. These materials isolate the steel from aggressive media but have poor strength and ductility and cannot be used as a structural material itself. As a protective coating, however, they allow application of steels with high strength and ductility which, if unprotected, are exposed to strong dissolution attack by LBE. The disadvantage of the coating concept is, however, that the coatings have no self healing ability and a fracturing or spallation of the coating would lead to a direct dissolution attack by the LBE of the uncovered part of the steel. This is the main problem with oxide, carbide and nitride coatings and it is enhanced by the fact that bad adherence may exist as well as stresses because of the differences in the thermal expansion. TiN, CrN and diamond like carbon coatings (DLC) of good adherence were obtained from Ion Bond AG, Olten, Switzerland, and employed for examination in the LBE of the CORWETT loop under stress at temperature of 350°C [Glasbrenner, 2004].

There are some attempts to employ ceramic coatings for the protection of steels against LBE. They include nitrides and borides of Ti and Zr, carbides of W, aluminium-magnesium spinel [Romano, 1963] and ZrO₂ + Y₂O₃ [Asher, 1977]. The layers are, however, not dense enough to inhibit cation and anion diffusion and are subjected to cracking and spalling. More development work is necessary.

9.2.3 Corrosion inhibitors in LBE

By definition inhibitors are substances which, when added to a chemical system in small amounts (in the order of only 10⁻³ wt.%), interact with the reactants to reduce the reaction rate. By this definition oxygen dissolved in LBE acts as such an inhibitor through the formation of a stable oxide film reducing the dissolution rate. Additions of other elements such as Zr or Ti to low oxygen LBE may provide an inhibitive effect, also [Hodge, 1970], [Shmatko, 1998]. A possible mechanism explaining this kinetic phenomenon is that Zr (or Ti) promotes the formation/creation of a thin, compact, adherent protective nitride layer being insoluble in the LBE deoxidised at first with Mg (approx. 5 × 10⁻² wt.%) acting as a getter [Hodge, 1970]. If enough nitrogen is present in the steel, protective TiN or ZrN films will form at first. After consuming all the nitrogen (most structural steels contain nitrogen in the order of several ppm), in the second step TiC and ZrC films will start to grow [Ilincev, 2002]. The existence of such films was proofed experimentally. Synergetic effects have not been reported. Creating protective films is also affected by the heat treatment. Fine nitrides are more uniformly distributed, e.g. nitrogen can diffuse faster. An indirect proof of the TiC, TiN or ZrC, ZrN, role is that inhibition is most effective on steels which are rich both C and N and, at the same time, characterised by a low content of Cr, Mo, V and other carbide and nitride-forming elements [Ilincev, 2002].

Inhibited corrosion rates of low-alloyed steels were examined as a function of temperature [Weeks, 1958] in comparison to reference samples without an inhibitor postulating that Zr/Ti solubilities in LBE are the most important factors affecting inhibition. Diffusion is of secondary importance. Stainless chrome, chrome–nickel and low-alloyed steels stabilised with strong carbide- and nitride-forming elements do not form protective films and thus they must corrode fast as in cases if no inhibitor was used (tests with reference samples).
Determining an optimal (in any case low!) concentration of the inhibitive additives and maintaining it at this low level during the whole loop operation and explaining the role of particular alloying elements in steels on the formation and mechanical stability of protective inhibitive films is still an obvious need. However, long-term tests on large devices are required before the inhibition method could be utilised on a large scale [Park, 2000].

Proper mixing procedures which assure a homogenous distribution of the inhibitor within the LM as well as maintaining its amount at a constant level during the whole loop operation are crucial here.

9.3 Corrosion examinations on alloys and coatings

9.3.1 Surface alloys

Several experiments with surface alloyed steel have been conducted in stagnant and flowing LBE with oxygen concentrations in the range of $10^{-4}$-$10^{-13}$ wt.%. The experimental conditions and results are listed in Tables 9.3.1 and 9.3.2.

As shown in Tables 9.3.1 and 9.3.2 most of the experiments were conducted with Al surface alloys produced by melt alloying with the GESA process and by pack cementation. In all GESA alloyed specimens stable protective oxide scales with no attack of LBE up to $650^\circ\text{C}$ and 10000 h are observed. This concerns austenitic as well as martensitic steels in an environment of stagnant LBE with $10^{-4}$ and $10^{-6}$ wt.% oxygen.

The same positive result was obtained for alloys produced by pack cementation up to $600^\circ\text{C}$ after 3000 h of exposure to stagnant LBE with about $10^{-4}$ wt.% oxygen. Examination of pack cementation alloys in stagnant LBE with oxygen concentrations below $10^{-8}$ wt.%, however, resulted in dissolution attack at temperatures above $500^\circ\text{C}$ after 1000 and 3000 h, respectively.

Looking at the experiments in the Prometey IPPE and CICLAD loops one can see satisfying protection behaviour of the Al-surface-alloyed steels at an oxygen concentration of $10^{-6}$ wt.% up to $600^\circ\text{C}$ [Müller, 2002, 2004], [Deloffre 2004] with the exception of the hot dipped steel, in which dissolution attack starts at $420^\circ\text{C}$ because of the high Al activity that leads to strong dissolution attack.

Some local corrosion processes in the pack cementation specimen near the sample holder are believed to be caused by LBE turbulences at the specimen tube holder [Deloffre, 2004].

9.3.2 Bulk alloys

Numerous experiments are conducted on steels alloyed with Si especially in the low concentration region up to 3 wt.%. The first experiments reported on austenitic steels containing up to 3 wt.% Si result in a low oxide scale thickness which levels up to 20 μm after 12000 h of exposure to LBE in a narrow region around $10^{-6}$ wt.% oxygen at $550^\circ\text{C}$ [Gorynin, 1999]. The same steel without Si addition reaches an oxide thickness > 80 μm at these conditions. Another experiment with the steel SX (Fe, 17.6Cr 4.8Si) at $550^\circ\text{C}$ shows a thin protective SiO$_2$ scale at the surface after 3000 h in LBE with saturated oxygen content [Kurata, 2005]. Although this is a desired result, the way can not be followed because above 1.5-2 wt.% of Si the steel impact strength decreases rapidly due to embrittlement [Gorynin, 1999] and the resistance against radiation damage decreases.
Systematic investigations of the influence of Si on surface protection in LBE with oxygen activities below that for the Fe/Fe$_3$O$_4$/FeO stability range showed the importance of Cr concentrations in steel [Ballinger, 2003], [Lim 2006]. While Si concentrations of up to 3.8 wt.% have no positive effect on protection of low Cr martensitic steel, in 12-18 Cr martensitic steel the thickness of the protective spinel oxide scale is drastically decreased with increasing Si concentration up to 2.25 wt.%. It is believed that a network of precipitated SiO$_2$ and Fe$_2$SiO$_4$ localised beneath the Cr rich oxide layer forms a barrier for diffusion of oxygen into the steel matrix [Lim, 2006].

A review on the experiments conducted is given in Table 9.3.3.

9.3.3 Coatings

Only few experiments with protective coatings have been conducted. The experiments in stagnant LBE are listed in Table 9.3.4 and those in flowing LBE are listed in Table 9.3.5.

The test with the FeCrAlY coating with GESA treatment was carried out under controlled oxygen concentration, and did not lead to a dissolution attack after 5000 h at 550 and 650°C in LBE with $10^{-6}$ wt.% oxygen [Weisenburger, 2005]. The alumina scale on the surface was very thin and did not show visible scale growth.

Nb coated on the surface of EUROFER97 and T91 steel did not react with LBE under strongly reducing conditions at 480°C during 1000 h [Benamati, 2004]. This is due to the fact that the solubility of Nb in LBE is very low. Nb coating with an Nb$_2$O$_5$ oxide scale produced by Nb anodisation is also resistant against attack by LBE in the temperature range of 450-500°C. Appropriate oxygen potential control is required in this case to prevent Nb$_2$O$_5$ decomposition. Experiments with W in LBE indicate that W as a coating is not compatible if the LBE is saturated with oxygen. A 50 μm thick reaction layer of WO$_3$ and Pb-W complex oxide covers the surface after 2000 h at 520°C [Benamati, 2004]. The same is expected to happen for Mo in this environment. Other experiments with coatings in LBE with no defined oxygen concentration level result in bad performance of the metal coatings, also of W and Ta, independent of the production process by plasma spraying, flame spraying, CVD or electrochemical deposition with the exception of Mo plasma sprayed on Croloy [Asher, 1977]. The other coatings suffered from cracking and spalling.

Experiments have been carried out at the relatively low temperature of 350°C to examine the influence of stresses on TiN, DLC and CrN coatings. They show diminishing of the protection behaviour as opposed to the unstressed conditions. Only TiN was not influenced by stresses and showed neither dissolution attack nor formation of cracks [Glasbrenner, 2004, 2005]. The results obtained in the experiments can be described as follows:

- Static load on CrN caused corrosion attack by LBE. This was not the case when the exposure tests were carried out without any static pressure. Hence, the stress has a negative influence to the compatibility of this layer.
- There seems to be no chemical interaction between LBE and the unstressed DLC layer. But at a static stress of 150 MPa a degradation of the layer and change in thickness occurred. The compression seems to be more effective than tension. In the areas with destroyed layer parts the specimen was affected by LBE.

Exposure of TiN coated specimens up to 6000 h in LBE revealed the most promising results. This coating is not influenced by LBE with and without static stresses up to 200 MPa.
9.4 Concluding remarks

Application of LBE with an oxygen concentration that ensures formation of magnetite on the steel surface is the first choice for realisation of a LBE cooled nuclear installation. The concentration must, however, be lower than that at which precipitation of PbO takes place. This would provide protective conditions especially for the low temperature parts. However at elevated temperatures this method of steel protection fails because of extensive steel corrosion by oxidation without sufficient prevention of dissolution attack by LBE. Therefore, structural parts exposed to high thermal loads like cladding tubes, which could reach temperatures above 500°C, need additional protection measures. It can be concluded at this point that austenitic and martensitic steel alloyed by GESA and austenitic steels alloyed by the pack cementation process and by foil melting fulfil as well as steels alloyed with Si the requirements concerning corrosion protection against the LBE attack up to 600°C if the oxygen concentration in LBE is between $10^{-4}$ and $10^{-6}$ wt.%. From the results obtained with pack cemented steels in LBE containing less than $10^{-8}$ wt.% oxygen, however, it seems, that the oxygen activity above 500°C gets low enough to allow dissolution attack on FeAl before a stable alumina scale is developed because the proceeding of this process depends strongly on the oxygen concentration in the surrounding LBE.

Alloying Al into the surface causes very thin, slowly growing oxide scales that prevent steel oxidation and dissolution attack by LBE. Additionally, the self healing in case of oxide scale defects that may occur during thermo cycling is expected.

Successful methods of alloying Al into the steel surface are:

- melt alloying by GESA and pack cementation for austenitic steels;
- FeCrAlY coating with subsequent alloying by GESA for martensitic and austenitic steels as well.

It is of advantage that the pack cementation and the FeCrAlY coating processes are already performed on an industrial level. Therefore, this process should be favoured. This holds as well for steels alloyed with Si during fabrication.

Coatings with metals of low solubility in LBE, e.g. Mo, and of nitrides and carbides should be excluded because they would require very low oxygen activities and would leave uncoated low temperature parts unprotected.

The use of oxide coatings, e.g. alumina, which would allow application of LBE with appropriate oxygen concentration must be excluded because of expected adhesion problems and because of absence of a self healing of defects.

For a final judgement of the suggested protection processes additional examination is required on:

- long-term behaviour;
- self healing properties;
- mechanical properties;
- behaviour under irradiation;
- influence of fretting on the protective layer.
<table>
<thead>
<tr>
<th>Method of surface alloying</th>
<th>Liquid metal/alloy</th>
<th>Test facility</th>
<th>Temp [°C]</th>
<th>Oxygen conc. [wt.%]</th>
<th>Time period [h]</th>
<th>Steel</th>
<th>Results</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-GESA</td>
<td>Pb</td>
<td>COSTA</td>
<td>550</td>
<td>10^{-6}</td>
<td>1500, 2500</td>
<td>1.4970, OPTIFER IVc</td>
<td>Thin protective layers.</td>
<td>[Müller, 2000, 2004]</td>
</tr>
<tr>
<td>Al-GESA</td>
<td>PbBi</td>
<td>COSTA</td>
<td>500, 550, 600, 650</td>
<td>10^{-4}, 10^{-6}, 10^{-8}</td>
<td>3000, 5000, 10000</td>
<td>316L, 1.4970, ODS, P122, OPTIFER IVc</td>
<td>Protective layers at all temperatures for 10000 h results for 10^{-8} wt.% at 650°C not yet available.</td>
<td>[Müller, 2004, 2004c]</td>
</tr>
<tr>
<td>FeAl by pack cementation</td>
<td>PbBi</td>
<td>COLIMESTA</td>
<td>350, 500, 600</td>
<td>10^{-9} - 10^{-8}</td>
<td>3000</td>
<td>316L, T91</td>
<td>Protective layers up to 500°C. At 600°C partial destruction of the alloyed layer occurred with consequent dissolution attack.</td>
<td>[Deloffre, 2004]</td>
</tr>
<tr>
<td>Pack cementation + oxidation</td>
<td>PbBi</td>
<td>COLIMESTA</td>
<td>350, 500, 600</td>
<td>10^{-9} - 10^{-8}</td>
<td>3000, 10000</td>
<td>316L (up to 10000 h at 350-500°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pack cementation + Al₂O₃ disposal by pyrosol</td>
<td>PbBi</td>
<td>COLIMESTA</td>
<td>350, 500, 600</td>
<td>10^{-9} - 10^{-8}</td>
<td>3000, 10000</td>
<td>316L (up to 10000 h at 350-500°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pack cementation</td>
<td>PbBi</td>
<td>IPPE facilities</td>
<td>470, 600</td>
<td>2.5<em>10^{-4} 9</em>10^{-4} 4<em>10^{-9} 4.3</em>10^{-13}</td>
<td>1000</td>
<td>316L</td>
<td>Protective at 10^{-4} wt.%, deep cracks at low oxygen concentrations.</td>
<td>[Deloffre, 2004]</td>
</tr>
<tr>
<td>FeAl by pack cementation</td>
<td>PbBi</td>
<td>JAERI facility</td>
<td>450, 550</td>
<td>Saturated</td>
<td>3000</td>
<td>F82H, Mod. 9Cr-1Mi, JPCA, 410SS, 430SS, 2.25Cr-1Mo</td>
<td>Layer produced by pack cementation exhibited corrosion resistance, while hot dipped samples showed a severe corrosion attack</td>
<td>[Kurata, 2004]</td>
</tr>
</tbody>
</table>
Table 9.3.2. Experimental verification of surface alloys with flowing LBE

<table>
<thead>
<tr>
<th>Method of surface alloying</th>
<th>Liquid metal/alloy</th>
<th>Test facility</th>
<th>Temp. [°C]</th>
<th>Oxygen conc. [wt.%]</th>
<th>Time period [h]</th>
<th>Steel</th>
<th>Results</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-foil diff.</td>
<td>PbBi</td>
<td>Prometey</td>
<td>420</td>
<td>10⁻⁶</td>
<td>4000 7500</td>
<td>316L, 1.4970</td>
<td>FeAl on the surface forms stable, thin alumina layer.</td>
<td>[Müller, 2004b]</td>
</tr>
<tr>
<td>Hot dipped Al 12 at.% Si</td>
<td>PbBi</td>
<td>Prometey</td>
<td>420</td>
<td>10⁻⁶</td>
<td>4000 7500</td>
<td>316L, 1.4970</td>
<td>Dissolution of the Al layer starts at 420°C and is completed at 600°C (pure Al at the surface).</td>
<td>[Müller, 2002, 2004b]</td>
</tr>
<tr>
<td>Pack cementation</td>
<td>PbBi</td>
<td>CICLAD</td>
<td>400</td>
<td>10⁻¹¹-10⁻¹²</td>
<td>500</td>
<td>316L</td>
<td>Localised attacks on the coating, but only at external parts.</td>
<td>[Deloffre, 2004]</td>
</tr>
<tr>
<td>Pack cementation</td>
<td>PbBi</td>
<td>IPPE (1.3 m/s)</td>
<td>470</td>
<td>10⁻⁶</td>
<td>1000</td>
<td>316L</td>
<td>No damage or modification of the coating up to 600°C. Near the sample holder some local corrosion probably because of PbBi turbulences there.</td>
<td>[Deloffre, 2004]</td>
</tr>
<tr>
<td>Al-GESA</td>
<td>PbBi</td>
<td>CORRIDA</td>
<td>550</td>
<td>10⁻⁶</td>
<td>5000</td>
<td>ODS, P122</td>
<td>No reaction, thin alumina scales.</td>
<td>[FZK], [Schroer, 2004]</td>
</tr>
</tbody>
</table>
Table 9.3.3. Experimental verification of Si-bulk alloys with LBE

<table>
<thead>
<tr>
<th>Steel</th>
<th>Si conc.</th>
<th>Pb/PbBi</th>
<th>Temp. [°C]</th>
<th>Oxygen conc. [wt.%]</th>
<th>Time [h]</th>
<th>Stag. or flow.</th>
<th>Results</th>
<th>Test facility</th>
<th>Lit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>JPCA 316 SS SX</td>
<td>0.5/0.69/4.8</td>
<td>PbBi</td>
<td>450 + 550</td>
<td>Saturated</td>
<td>3000</td>
<td>Stag.</td>
<td>450°C: all steels are protected 550°C: JPCA, 316SS dissolution attack. SX is protected by a thin SiO₂ scale</td>
<td>No name</td>
<td>[Kurata, 2004]</td>
</tr>
<tr>
<td>EI 852 EP 823</td>
<td>1.5-2 2</td>
<td>PbBi</td>
<td>560 620</td>
<td>7·10⁻⁶-1·10⁻⁶ to 5·10⁻⁶-8·10⁻⁷</td>
<td>8000 + 12000 2300-2598</td>
<td>1.8-2 1.2-1.5 2 m/s</td>
<td>Both steels are protected by a thin oxide layer of 3-5 μm.</td>
<td>SMI, SVR, TSU-1M (bei IPPE)</td>
<td>[Yachmenyov, 1999]</td>
</tr>
<tr>
<td>SUH3 (11Cr) NTK04L (18Cr)</td>
<td>2 3.34Al</td>
<td>PbBi</td>
<td>550</td>
<td>2·10⁻⁸</td>
<td>1000</td>
<td>1 m/s</td>
<td>In general the weight loss decreases with increasing Cr content.</td>
<td></td>
<td>[Kondo, 2004]</td>
</tr>
<tr>
<td>Austenite Martensite</td>
<td>2 + 3 2</td>
<td>PbBi</td>
<td>400 550 600 650</td>
<td>10⁻⁶/4·10⁻⁶/4·10⁻⁷/ 10⁻⁴</td>
<td>3000-12000</td>
<td>Stag. 4-6 m/s</td>
<td>Double oxide layer decreases with increasing Si content. Dissolution attack at &lt; 10⁻⁸ wt.%.</td>
<td></td>
<td>[Gorynin, 1999]</td>
</tr>
<tr>
<td>Fe-Si alloys</td>
<td>1.24/ 2.55/ 3.82</td>
<td>PbBi</td>
<td>400, 500, 600, 700</td>
<td>Below Fe/Fe₂O₃/FeO formation</td>
<td>100-1000</td>
<td>0.2 m/s</td>
<td>No effect of Si on surface protection.</td>
<td>Forced convection corrosion cell</td>
<td>[Loewen, 2004, 2005]</td>
</tr>
<tr>
<td>Fe12Cr Fe2.25Cr Fe18Cr Fe18Cr Fe18Cr</td>
<td>0.5 1.25 0.5 1.25 2.55</td>
<td>PbBi</td>
<td>600</td>
<td>Below Fe/Fe₂O₃/FeO formation</td>
<td>100-300</td>
<td></td>
<td>Reduction of oxide layer thickness with increasing Si content.</td>
<td></td>
<td>[Lim, 2005]</td>
</tr>
<tr>
<td>EP823</td>
<td>1.8</td>
<td>PbBi</td>
<td>300-470</td>
<td>10⁻⁶</td>
<td>3116</td>
<td>2 m/s</td>
<td>The presence of Si in EP823 reduces the oxide growth rate, which improves the resistance to oxidation.</td>
<td>CU-1M (IPPE)</td>
<td>[Barbier, 2001]</td>
</tr>
</tbody>
</table>
Table 9.3.4. Experimental verification of coatings in stagnant LBE

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb by galvanic deposition</td>
<td>PbBi</td>
<td>ENEA, Brasimone Laboratory</td>
<td>480</td>
<td>Mg in LBE, H2 bubbling</td>
<td>1000</td>
<td>EUROFER97, T91</td>
<td>No reaction visible</td>
<td>[Benamati, 2004]</td>
</tr>
<tr>
<td>Nb by magnetron sputtering</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb by galvanic deposition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb by magnetron sputtering</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


### Table 9.3.5. Experimental verification of coatings in flowing LBE

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>FeAl (CVD)</td>
<td>PbBi</td>
<td>CORRWET</td>
<td>350</td>
<td>Sat.</td>
<td>6000</td>
<td>T91</td>
<td>No dissolution attack, no spallation of the surface layer.</td>
<td>[Galsbrenner, 2004]</td>
</tr>
<tr>
<td>TiN (CVD)</td>
<td>PbBi</td>
<td>CORRWETT</td>
<td>350</td>
<td>Sat.</td>
<td>6000</td>
<td>T91</td>
<td>No dissolution attack, no spallation of the layer.</td>
<td>[Galsbrenner, 2004]</td>
</tr>
<tr>
<td>CrN (PVD)</td>
<td>PbBi</td>
<td>CORRWETT</td>
<td>350</td>
<td>Sat.</td>
<td>6000</td>
<td>T91</td>
<td>No dissolution attack, no spallation of the surface layer.</td>
<td>[Galsbrenner, 2004]</td>
</tr>
<tr>
<td>DLC (low temperature coating process)</td>
<td>PbBi</td>
<td>CORRWETT</td>
<td>350</td>
<td>Sat.</td>
<td>6000</td>
<td>T91</td>
<td>No dissolution attack, no spallation of the surface layer.</td>
<td>[Galsbrenner, 2004]</td>
</tr>
<tr>
<td>FeCrAlY + GESA</td>
<td>PbBi</td>
<td>IPPE loop</td>
<td>500, 550, 600</td>
<td>10^-6</td>
<td>5000</td>
<td>1.4970</td>
<td>No dissolution attack, no spallation of the surface layer.</td>
<td>[Ballinger, 2004]</td>
</tr>
<tr>
<td>WC, Al2O3, Mo, Ti</td>
<td>Pb</td>
<td></td>
<td>Up to 1127</td>
<td>Reduced</td>
<td>100-120</td>
<td>Incolloy 800, X15CrNiSi 25 20</td>
<td>All coatings except Ti protected the steels; because of the different expansion coefficient of steel and protective layer, no tight interlocking and some cracks were observed.</td>
<td>[Block, 1977]</td>
</tr>
<tr>
<td>Mo flame spraying</td>
<td>Pb</td>
<td></td>
<td>700-720</td>
<td>Reduced</td>
<td>Up to 1344</td>
<td>Croloy</td>
<td>Coatings appeared to be unsatisfactory since the coating did nit remain intact. The bad performance of most coatings did not seem to depend on whether the coating was applied. But Mo plasma sprayed and Al show some promise.</td>
<td>[Asher, 1977]</td>
</tr>
<tr>
<td>Mo und ZrO+Y2O3 plasma spraying</td>
<td>Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Croloy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo chemical deposition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Croloy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta electrochemical</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Croloy</td>
<td>Stainless steel</td>
<td></td>
</tr>
<tr>
<td>Ta vapour phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Croloy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al pack cementation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Croloy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb by magnetron sputtering</td>
<td>PbBi</td>
<td>LECCOR</td>
<td>10^-10</td>
<td></td>
<td>T91</td>
<td></td>
<td>No reaction visible.</td>
<td>[Benamati, 2004]</td>
</tr>
</tbody>
</table>
REFERENCES


Deloffre, Ph., F. Herbert, C. Delisle, C. Blanc, S. Poissonnet (2003), *Behavior of the Aluminized T91 Martensitic Steel and 316 Austenitic Steel on Contact with Static and Dynamic Pb-Bi*, Rapport Technique SCCME, RT-SCCME 584.


FZK/JNC report, forthcoming.


Glasbrenner, H., F. Gröschel (2005), presented during *IWSMT-7*, Thun, Switzerland, 29 May-3 June.


Weeks, J.R., D.H. Gurinsky (1958), Liquid Metals and Solidification, ASM, pp. 106-161


10. Introduction

This chapter is an introduction into the field of momentum and heat transfer in low Prandtl number fluids. In order to read this chapter a basic knowledge in fluid dynamics and thermodynamics is required. To limit the content not all formulas for technical configurations are listed; therefore much better literature sources are available in engineering libraries or other specific sources.

The first section illuminates the specific characteristics of the liquid metals, which represent the largest class of low Prandtl number fluids. Rather specific low Prandtl number fluids like ferromagnetic fluids or metal/oil suspensions are not considered in this context. It is clearly dedicated to the single phase thermal-hydraulics of liquid metals obeying the Newtonian law. The terminology used in this report as well as the conservation equations are part of Chapter 2.

In the sections three and four are restricted to the laminar momentum and heat transfer although they are not of major importance in technical applications they act in many situations as the upper or lower limit appearing in a technical set-up. Here, first the momentum transfer is described, because the convective heat transport is always coupled with the simultaneously appearing momentum transport. Analytic solutions like for tube or plate flow as well as self-similar solutions of the boundary layer equations and coupled approximate solutions are sketched. Especially the latter can be used to perform technically relevant problem solutions. For some technical configurations formulas or literature sources are given. Both paragraphs deal solely with the technically most relevant case, namely the forced convective flow, in which the flow is controlled by a shaping of the duct or by a supplied pressure gradient.

The sections five and six deal with the turbulent momentum and energy transport through channels and ducts. Due to the importance of this field most of the space is dedicated to it. Natural or buoyant convection are in many applications superposed to the forced convective thermal energy transport phenomena. These types of flows are called mixed convective flows and are analytically not accessible and even a numerical treatment requires a lot of effort. Hence, within the section six the author tries to indicate for which dimensionless parameter set a forced turbulent thermal energy transport exists and where the transition region starts. Buoyant or natural convection both for the laminar and the turbulent energy exchange are not considered in this context. Although two-phase flows as well as free surface flows gain more and more importance in technical applications this rather specific topic is also not treated in the framework of this collection.
10.2 Specific features of liquid metals

Liquid metals are considered in many nuclear and non-nuclear processes associated with thermal-hydraulic aspects. In the nuclear field liquid metals are both used in fission and fusion concept studies. While in the nuclear fusion lithium or lithium alloys allow to merge the fuel generation problem with the heat removal from the fusion reaction, see e.g. [Malang, et al., 1992] in the nuclear fission the use of liquid metals is much broader. In the fast breeder concept for instance sodium is used as coolant while in newer breeder concepts often lead or lead alloys are used, since they ensure compared to sodium in any case that no positive void coefficient appears. A comprehensive study on the fuel and coolant aspects as well as their advantages and disadvantages may be taken from [David, 2005]. Also in the non-nuclear energy generation liquid metals are used as heat transfer medium in solar plants, where the sunlight is reflected by numerous mirrors onto a heat exchanger operated with liquid metals, see [Benemann, 1996]. In refinery and casting processes of metals like steel, copper, tin, aluminium etc., as well as glasses, which behave in the molten condition similar like liquid metals, the same heat transfer problems appear as in the power generation field.

The main difference between the metals and the other media is that they have a significantly higher thermal conductivity \( \lambda \) (W/mK) and lower specific heat capacity \( c_p \) [J/(kgK)]. In case of the heavy liquid metals like lead, lead-alloys or mercury often the kinematic viscosity \( \nu \) (m²/s) is considerably smaller than that of e.g. air or water. The thermal conductivity combined with the specific heat capacity can be compressed in a characteristic number the so-called Prandtl number \( Pr \). The Prandtl number is an essential non-dimensional parameter in convective heat transfer problems. The physical sense of the Prandtl number is that it weights the transport coefficients of momentum to that of thermal energy. Thus, the Prandtl number describes the ratio of momentum diffusion to the thermal transport in the fluid and it is defined as:

\[
Pr = \frac{\rho \nu c_p}{\lambda} = \frac{\nu}{\kappa} \quad \text{with} \quad \kappa = \frac{\lambda}{\rho c_p}
\]

where \( c_p \) is the specific heat capacity, \( \rho \) the density (kg/m³) and \( \lambda \) the thermal conductivity. \( \kappa \) is often called in textbooks the temperature conductivity or thermal diffusivity. In contrast to gases or light liquid the heat capacity hardly depends on the pressure.

While engine oils have usually Prandtl number of the order O(10²-10⁶) and “conventional” media like air or water reveal an order of O(1) Prandtl number the liquid metals exhibits significantly smaller Prandtl numbers in the range \( Pr = 10^{-3}-10^{-2} \). Table 10.2.1 shows the Prandtl number of e.g. mercury compared to air water or engine oil for different temperatures. There exists no Newtonian fluid in the range between the liquid metals and the gases for e.g. \( 0.05 < Pr < 0.5 \).

**Table 10.2.1. Typical Prandtl number for different fluids from [Beitz & Küttner, 1986]**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mercury</th>
<th>Air</th>
<th>Water</th>
<th>Engine oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°C</td>
<td>0.0288</td>
<td>0.72</td>
<td>13.6</td>
<td>4.710⁴</td>
</tr>
<tr>
<td>20°C</td>
<td>0.0249</td>
<td>0.71</td>
<td>7.02</td>
<td>1.010⁴</td>
</tr>
<tr>
<td>100°C</td>
<td>0.0162</td>
<td>0.70</td>
<td>1.74</td>
<td>2.610²</td>
</tr>
</tbody>
</table>

Let us consider a flow of a Newtonian fluid with the temperature \( T_0 \) over a semi-infinite plate with the constant temperature \( T_w \). In Figure 10.2.1 such a configuration is illustrated for fluids with \( Pr << 1, Pr \sim 1 \) and \( Pr >> 1 \). Case (a) refers to liquid metals, which have good conductivity and a low viscosity, it is \( Pr << 1 \). Here the thickness of the viscous boundary layer \( \delta \), is negligibly small and to
estimate the temperature boundary layer the velocity profile can be replaced by \( u_0(x) \). In gas or water flows the thickness of the thermal and the viscous boundary layer are of the same order of magnitude, it is \( Pr \sim 1 \). Liquid like cool water (\(<20^\circ C\)) and especially oils have poor thermal conductivity but their viscosity is relatively large, as shown in case (c). Here the viscous boundary determines almost the whole flow field.

In forced convective systems under laminar flow conditions, molecular conduction of heat expressed by the Prandtl number controls the thermal energy transfer process, irrespective of whether the coolant is a liquid metal or any other Newtonian fluid. Hence, there is no fundamental difference between the thermal behaviour of the three types of fluids described above under these conditions. And accordingly non-dimensional correlations developed to describe the heat transfer performance can be generally applied equally well to liquid metals in spite of their low Prandtl number.

Under turbulent flow conditions, however, eddy conduction of heat becomes important and the process of heat transfer is determined by both molecular and eddy conduction over the various flow regions in the fluid stream. While in ordinary fluids like air and water molecular conduction is only of importance near the wall (in the viscous sublayer), in a liquid metal the magnitude of the molecular conductivity is of the same order as that of the eddy conductivity. Thus, the molecular conduction is felt by the flow not only in the boundary layer but also to a significant extend in the turbulent core of the fluid stream. Therefore, the fundamental details of the heat transfer mechanism in liquid metals differ significantly from those observed for instance in air and as a result relationships (or correlations) developed to determine the heat transfer coefficients for turbulent flows obtained in those fluids cannot be used.

A further consequence of the even greater importance of molecular conduction of thermal energy in turbulent liquid metal flow is that the concept of the hydraulic diameter cannot be used so freely to correlate heat transfer data from systems which differ in configuration but retain a similar basic flow pattern. As an example in \( Pr \sim 1 \) fluids basic heat transfer data for flow through circular pipes can be used to predict Nusselt numbers \((Nu)\) for flow parallel to a rod bundle by evaluating the hydraulic diameter for the latter and using this in the non-dimensional correlations for the circular tube. Such methods are found to be invalid for liquid metal systems, and accordingly theoretical, numerical or experimental heat transfer relationships must be developed to deal with each specific configuration, see [Reed, 1987] or [Dwyer, 1976].

Also a lot of effort has been dedicated to evaluate heat transfer coefficients in standard geometries in the recent years the available liquid metal heat transfer data show quite a bit of scatter. Several phenomena have been proposed to explain the scatter and the corresponding lack of correlation with
numerical predictions or theoretical approximations. They include: non-wetting or partial wetting of the fluid-solid interface, gas entrainment, the possibility of oxide formation or other surface contaminants, and mixed convection effects. Especially, the latter three influences the heat transfer considerably and by tracking numerous literature sources published in the past decades it turned out that they are mostly responsible for the existence of the large scatter. In this context it should be mentioned that for many liquid metal experiments a detailed description of the thermal and viscous boundary conditions is incomplete, which makes it difficult to judge about the applicability of the obtained data to draw estimation to more general geometries. And, even if great care is take on the boundary conditions in a pre- and post-test analyses of the experiment, in the heated state asymmetries in the set-up may appear leading to a co-existence between mixed and forced convection suggesting different heat transfer coefficients than under “clean” conditions, see [Lefhalm, et al., 2004].

Following an extensive amount of experimental investigations on the effects of wetting on the liquid metal heat transfer a general consensus has been reached on the subject. This is that wetting or lack of wetting, in or of itself, does not significantly affect liquid metal heat transfer. However, non-wetting combinations of liquid metals and solid surfaces can suffer more readily from gas entrainment problems and at elevated temperatures of oxidation at the solid liquid interface; impurities and particles can more easily become trapped at a non-wetting solid-liquid interface, thus reducing heat transfer. Hence care should be taken to avoid these problems in system designs. Finally, in liquid metal systems, uniform wall temperature boundary conditions (although difficult to obtain in the experiment) yield lower Nusselt numbers than constant wall heat flux boundary conditions for the same Peclet number. This is in contrast to $Pr \sim 1$-fluids, in which the two boundary conditions make only a little difference in the Nusselt number.

Related to the heavy liquid metals for many thermal-hydraulic configurations often no Nusselt number correlation exists. However, a lot of experiments in rather generic geometries were conducted for the sodium cooled fast breeder and in the context of the fusion engineering community using alkali metals as operation fluid. In many cases the Prandtl number of the individual fluids is close to the heavy liquid metals as shown in Figure 10.2.2. Nevertheless, great care has to be taken on the validity of the chosen heat transfer correlation even if the Prandtl number matches the heavy liquid metal considered, because the viscosity of the heavy liquid metals is considerably smaller than that of the alkali metals.

**Figure 10.2.2. Molecular Prandtl number as a function of temperature in [°C] for different fluids**

The thermophysical data for lead and lead-bismuth are taken from this book, while the data for sodium, the eutectic sodium-potassium alloy ($Na^{22}K^{78}$) are from [Foast, 1972], mercury (Hg) from [Lyon, 1952], lithium from [Addison, 1984], lead-lithium (Pb$^{83}$Li$^{17}$) from [Schulz, 1986] and [Smith, et al., 1984] and gallium-indium-tin from [Barleon, et al., 1996].
By multiplying the hydraulic Reynolds number $Re$ with the Prandtl number $Pr$ the Peclet number $Pe$ is obtained which can be conceived as the ratio of the convective heat transport versus the molecular conduction. Both the Reynolds number and the Peclet number are defined as:

$$Re = \frac{u_0 \cdot d}{v} \quad \text{and} \quad Pe = Re \cdot Pr = \frac{u_0 \cdot d}{\kappa}$$  \hspace{1cm} (10.2)

where $u_0$ is a characteristic velocity of the flow configuration considered and $d$ a characteristic length scale of the problem. The Nusselt number correlations experimentally obtained can only then used for a heat transfer assessment or a transfer from an alkali metal to the heavy liquid metals if both Prandtl number and the valid Peclet number regime coincide.

### 10.3 The conservation equations

Within the context of this chapter we restrict ourselves to the consideration of flows in channels or closed cavities without the entrainment of an additional mass source or a mass transfer between different species.

Consider the flow of a single phase and single component fluid in a fixed control volume, then whole mass flow entering the volume must leave the volume. This is expressed by the continuity equation, which describes the conservation of mass. Because liquid metals below their boiling point are almost incompressible ($\rho = \text{const.}$) the continuity equation for them can be expressed by

$$\nabla \cdot \vec{u} = 0 \quad \text{or vectorial} \quad \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0$$ \hspace{1cm} (10.3)

where $\vec{u}$ is the velocity vector composed of the velocity components $(u,v,w)$ in $x$, $y$, and $z$-direction respectively and $(\nabla \cdot)$ is the divergence operator.

The dynamic behaviour of fluid motion is governed by a set of equations called the momentum equations or the equation of motion. The derivation considering a defined control volume is similar to that of the continuity equations. The momentum equations can be written in the following form:

$$\rho \left( \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} \right) = \rho f_x + \frac{\partial \sigma_{ux}}{\partial x} + \frac{\partial \tau_{ux}}{\partial y} + \frac{\partial \tau_{ux}}{\partial z} \hspace{1cm} (10.4)$$

$$\rho \left( \frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + w \frac{\partial v}{\partial z} \right) = \rho f_y + \frac{\partial \sigma_{vy}}{\partial x} + \frac{\partial \tau_{vy}}{\partial y} + \frac{\partial \tau_{vy}}{\partial z}$$

$$\rho \left( \frac{\partial w}{\partial t} + u \frac{\partial w}{\partial x} + v \frac{\partial w}{\partial y} + w \frac{\partial w}{\partial z} \right) = \rho f_z + \frac{\partial \sigma_{wz}}{\partial x} + \frac{\partial \tau_{wz}}{\partial y} + \frac{\partial \tau_{wz}}{\partial z}$$

where $f = (f_x, f_y, f_z)$ is a body force being of gravitational, electrical or magnetic origin, $\sigma$ is the stress normal to the surface and $\tau$ the shear stress tangential to the sides of the control volume. It has been found experimentally that, to a high degree of accuracy, stresses in many fluids are related linearly to the rates of strain (derivatives of the velocity components). It can be shown, see e.g. [Lamb, 1945] or [Schlichting, 1979] that for Newtonian fluids the expressions are:
\[ \sigma_{xx} = -p + 2\mu \frac{\partial u}{\partial x} - \frac{2}{3} \mu \nabla \cdot \mathbf{u} ; \]
\[ \sigma_{yy} = -p + 2\mu \frac{\partial v}{\partial y} - \frac{2}{3} \mu \nabla \cdot \mathbf{u} ; \]
\[ \sigma_{zz} = -p + 2\mu \frac{\partial w}{\partial z} - \frac{2}{3} \mu \nabla \cdot \mathbf{u} ; \]
\[ \tau_{xy} = \tau_{yx} = \mu \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) ; \quad \tau_{xz} = \tau_{zx} = \mu \left( \frac{\partial w}{\partial x} + \frac{\partial u}{\partial z} \right) ; \quad \tau_{yz} = \tau_{zy} = \mu \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \]

where \( \mu = \rho \nu \) is the dynamic viscosity of the fluid and \( p \) the pressure. Substituting the Eq. (10.5) into (10.4) yields the full momentum equations, which are called the Navier-Stokes equations. Nearly all analytical investigations involving viscous fluids are based on them. They are general in the sense that they are valid for compressible Newtonian fluids with varying viscosity.

When the density and the viscosity are constant – that is, when the fluid is incompressible and the temperature variations are small – the Navier-Stokes equations simplify to:

\[ \rho \left( \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} \right) = \rho f_x - \frac{\partial p}{\partial x} + \mu \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) ; \]
\[ \rho \left( \frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + w \frac{\partial v}{\partial z} \right) = \rho f_y - \frac{\partial p}{\partial y} + \mu \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2} \right) ; \]
\[ \rho \left( \frac{\partial w}{\partial t} + u \frac{\partial w}{\partial x} + v \frac{\partial w}{\partial y} + w \frac{\partial w}{\partial z} \right) = \rho f_z - \frac{\partial p}{\partial z} + \mu \left( \frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2} \right) \]

or in the vectorial notation
\[ \frac{du}{dt} = f - \frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{u} \]

where \( \nabla^2 = \nabla \cdot \nabla \) is the Laplacian operator given by \( \nabla^2 = (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) \).

Any fluid flow problem which involves the determination of the velocity components and the pressure distribution as a function of the spatial co-ordinates and the time requires simultaneously the solution of the continuity equation and the Navier-Stokes equations under the specific boundary and initial conditions. Although these set of equations are in most cases too complex to be solved analytically they may be solved by numerical means. Nevertheless, there exist some cases where the nature of the flow is such that they can be simplified considerably for an analytical solution.

A similar approach as for momentum and continuity equation derivation can be applied to deduce the energy equations. This derivation implies the first law of thermodynamics, which couples the thermal energy with the work done by the system and the total internal energy of the control volume. The complete derivation of the energy equation is described in the textbooks by [Keenan, 1941], [Van Vylen and Sonntag, 1979] or [Jischa, 1982]. The thermal energy equation finally reads to:

\[ \rho \frac{du}{dt} = \nabla \cdot (\lambda \nabla T) + \sigma_{xx} \frac{\partial u}{\partial x} + \sigma_{yy} \frac{\partial v}{\partial y} + \sigma_{zz} \frac{\partial w}{\partial z} + \tau_{xy} \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) + \tau_{xz} \left( \frac{\partial w}{\partial x} + \frac{\partial u}{\partial z} \right) + \tau_{yz} \left( \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \]
in which \( \lambda \) is the thermal conductivity of the fluid, \( u \) the internal energy and \( T \) the temperature. The internal energy is liked to the fluid enthalpy \( i \) by \( I = u + p/\rho \). The operator \( d/dt \) denotes the total derivative. If the relations for stress and strain acting upon a fluid element in a Newtonian fluid [Eq. (10.5)] are substituted into Eq. (10.7), it reduces to:

\[
\rho \frac{du}{dt} = \nabla \cdot (\lambda \nabla T) - p \nabla \cdot \mathbf{u} + \mu \Phi \\
\Phi = 2 \left[ \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial v}{\partial y} \right)^2 + \left( \frac{\partial w}{\partial z} \right)^2 \right] + \left[ \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right)^2 + \left( \frac{\partial w}{\partial y} + \frac{\partial u}{\partial z} \right)^2 + \left( \frac{\partial w}{\partial z} + \frac{\partial v}{\partial x} \right)^2 \right] - \frac{2}{3} (\nabla \cdot \mathbf{u})^2
\]

where \( u \) is the internal energy of the fluid per unit mass and \( \Phi \) is called the dissipation function. The first term on the right hand side represents the net rate of heat conduction to the fluid particle per control volume, the second term is the rate of reversible work done on the control volume and the last term is the rate at which viscous forces do irreversible work in form of e.g. viscous dissipation or viscous heating per unit volume.

If one considers an incompressible fluid with \( du = c_p dT \) the energy equation takes the form:

\[
\rho c_p \frac{dT}{dt} = \nabla (\lambda \nabla T) + \mu \Phi \\
\Phi = 2 \left[ \left( \frac{\partial u}{\partial x} \right)^2 + \left( \frac{\partial v}{\partial y} \right)^2 + \left( \frac{\partial w}{\partial z} \right)^2 \right] + \left[ \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right)^2 + \left( \frac{\partial w}{\partial y} + \frac{\partial u}{\partial z} \right)^2 + \left( \frac{\partial w}{\partial z} + \frac{\partial v}{\partial x} \right)^2 \right]
\]

Additionally, if the thermal conductivity \( \lambda \) is constant it reduces to:

\[
\frac{dT}{dt} = \frac{\lambda}{\rho c_p} \nabla^2 T + \frac{\mu}{\rho c_p} \Phi
\]

The continuity, Navier-Stokes and energy equations provide a comprehensive description of the thermal energy transfer in a flow field. These equations, however, present insurmountable mathematical difficulties due to the number of equations to be simultaneously satisfied and the presence of non-linear terms such as \( u \partial u/\partial x \). Because of these non-linearities, the superposition principle is not applicable and complex flows may not be compounded from simple flow as e.g. possible for potential flows, see [Schlichting and Truckenbrodt, 1960]. Exact solutions were obtained for some simple cases, where the nonlinear terms are either small (approximate solutions) or identically zero. This class of solution appears in slow motion or creeping flows and is important for the theory of lubrication. In most practical heavy liquid metal applications the nonlinear terms are most often of greater magnitude than the other terms in the Navier-Stokes equations. The hydraulic Reynolds number defined in Eq. (10.2) is a dimensionless quantity which measures the ratio of the inertia effects to the viscous effects in a fluid. Creeping flows are therefore characterised by small Reynolds numbers, whereas in most practical flows the Reynolds number is far above unity. Finally, two important observations are worth mentioning. First, the velocity and temperature fields will be coupled if the fluid has a temperature dependent density and/or viscosity. Secondly the temperature field can become similar to the field under certain conditions. If \( \nabla p = 0 \), \( \Phi = 0 \) and \( f = 0 \) and if \( Pr = 1 \) then the solutions for the velocity and temperature fields are similar, provided that the boundary conditions are also similar. But as shown in Section 10.2 for any liquid metal flow the molecular Prandtl number is far below unity so that a similarity of both fields does practically not appear.
10.4 Laminar momentum exchange

This subsection is dedicated to describe the basic concepts to treat the laminar momentum exchange. The main aim is to obtain the local friction coefficient $c(x)$ of a flow in a geometry and the main ideas for the simplification of the Navier-Stokes equations in terms of an asymptotic approach. The results obtained in this chapter are necessary to elaborate the difference between the laminar and the turbulent flow and they form the basis for the understanding of the heat transfer phenomena appearing in both types of flows.

The laminar momentum exchange of a steady two-dimensional flow of an incompressible fluid with a constant kinematic viscosity $\nu$ is governed by the following equations:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 ,$$

$$\frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial x} + \nu \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) ;$$

$$\frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{1}{\rho} \frac{\partial p}{\partial y} + \mu \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) .$$

This represents a system of partial non-linear differential equations of the elliptic type. A general solution does not exist and there are only a few exact solutions under rather restrictive boundary conditions like the channel or duct flow. Fortunately, most of the laminar momentum exchange processes can be simplified considerably. For large Reynolds numbers nearly all exchange processes take place in a thin layer, the so-called boundary layer. The boundary layer approximation is not restricted to flows over solid walls, also free jets or wake flows exhibit boundary layer character.

10.4.1 Channel or tube flow

Consider a steady planar fully developed flow in a duct as shown in Figure 10.4.1. Here fully developed means that the velocity component $u$ in $x$-direction does not change. Because $\partial u/\partial x = 0$ also $\partial v/\partial y = 0$, which means that the $v$-component of the velocity is constant. Excluding suction or blowing immediately yields that $v = 0$. For Eqs. (10.11)b, c the convective terms on the left side diminish and from the force balance (10.11)c only the expression $\partial p/\partial y = 0$ remains. Thus, the pressure $p$ depends only from the flow direction $x$ and the force balance in flow direction reads to:

$$\frac{dp}{dx} = \mu \frac{d^2 u}{dy^2} = \frac{d\tau}{dy} ,$$

and since $u$ is only a function of $y$ the partial derivative $\partial$ can be replaced by the simple derivative $d$. From the stress tensor only $\tau = \mu \partial u/\partial y$ remains. An integration immediately yields that the shear stress is linear and due to symmetry, which requires $\tau(y = H) = 0$ one obtains:

$$\tau_w = -\frac{dp}{dx} H^{10} .$$
This correlates the wall shear stress with the pressure gradient. In dimensionless form it reads to:

\[
\frac{\tau(y)}{\tau_w} = 1 - \frac{y}{H}
\]  

(10.14)

With \( \tau = \mu \frac{\partial u}{\partial y} \) and a further integration the velocity distribution is obtained. Setting \( u(y = H) = u_{max} \) yields:

\[
u_{max} = \frac{\tau_w H}{2\mu} = -\frac{dp}{dx} \frac{H^2}{2\mu} = \frac{\Delta p H^2}{2\mu L}
\]  

(10.15)

where \( \Delta p/L = -dp/dx \) is the pressure drop along the channel length \( L \). Finally the dimensionless velocity distribution reads to:

\[
\frac{u}{u_{max}} = \frac{y}{H} \left( 2 - \frac{y}{H} \right)
\]  

(10.16)

which is the classical parabolic Hagen-Poiseuille profile.

Figure 10.4.1. Shear stress and velocity distribution of a fully developed channel flow for a planar duct and a circular pipe

The same result is obtained for the fully developed laminar circular duct flow using the same procedure. Without describing the full details the following set is obtained for the configuration shown in Figure 10.4.1:

\[
\frac{\tau(r)}{\tau_w} = \frac{r}{R} \quad u(r) = \frac{\Delta p}{4\mu L} \left( R^2 - r^2 \right); \quad u_{max} = \frac{\Delta p R^2}{4\mu L} \quad \frac{u}{u_{max}} = 1 - \left( \frac{r}{R} \right)^2
\]  

(10.17)

Here, \( R \) is the radius of the pipe and \( r \) the radial co-ordinate.

The factor \( \frac{1}{2} \) is explained by the fact that in a tube flow compared to a channel flow a ratio the cross-section on which the pressure acts is twice as large as the surface on which the viscous forces act to compensate the pressure. The flow rate \( V \) in a circular tube can be calculated to:
It is important to note the dependencies $V \sim \Delta p/L$ and $V \sim R^4$. For the same applied pressure gradient an increase of the diameter by 10% yields an increase of the flow rate of 46%. If one defines a mean velocity $u_0$ by applying $u_0 = V/A$ one obtains $u_0 = \frac{1}{2} u_{\text{max}}$. For engineering purposes the pressure loss is one of the most interesting parameters. Taking $V = u_0 \pi R^2$ and using the diameter $D = 2R$, one gets for the pressure drop over a duct length of $L$:

$$
\Delta p = \frac{\rho}{2} \frac{L}{D} \frac{u_0^2}{Re}
$$

(10.19)

Defining a friction coefficient $c_L$ in the way $\Delta p = \rho/2 L/D u_0^2$ one obtains the friction law for a tube flow expressed by:

$$
c_L = \frac{64}{Re}
$$

(10.20)

Herein $Re$ is the hydraulic Reynolds number defined as $Re = u_0 D/v$, which can be conceived as a force ratio of the inertial forces versus the viscous ones. This shows simply, how the pressure drop and the friction coefficient depend on the Reynolds number. The Reynolds number is in all momentum exchange processes the only appearing variable. Thus, for all laminar flows the Reynolds number correlations of any other liquid can be used and transferred to heavy liquid metals.

### 10.4.2 Boundary layer equations

The basis for the derivation of the boundary layer equations is the equation set (10.11)a-c. Figure 10.4.2 shows the used local co-ordinate system and the observed velocity distribution. The order of thickness of the boundary layer is a priori not known; the following assessment is aimed to give an estimate on this magnitude.

**Figure 10.4.2. Co-ordinate system and observed velocity distribution**

First we introduce the dimensionless variables in the following way:

$$
x' = \frac{x}{L}; \quad y = \frac{y}{\delta(x)}; \quad u' = \frac{u}{u_0}; \quad p' = \frac{p}{\rho u_0^2}
$$

(10.21)
which are chosen in such a way that they are of order one in magnitude $O(1)$. In a next step the length $L$ and the mean velocity $u_0$ of the outer flow are taken as reference quantities. Further on there is:

$$v' = \frac{v}{u_0}; \quad \rho' = \frac{\rho}{\rho_0} = 1 \quad \text{(because $\rho = \text{const.}$)}$$  \hfill (10.22)

Introducing these variables into the continuity Eq. (10.11)a the following declaration can be made:

$$\frac{v}{u_0} \sim \frac{\delta}{L}$$  \hfill (10.23)

because $u'$, $x'$ and $y'$ are of $O(1)$. Introducing the variables into the Navier-Stokes Eq. (10.11)b in $x$-direction leads to the result that as determining parameter the Reynolds number appears, which characterises viscous flows. Returning to the assessment and postulating that the viscous terms are of the same order of magnitude as the inertial terms and the pressure force immediately yields that the thickness of the boundary layer scales as:

$$\frac{\delta}{L} \sim \frac{1}{\sqrt{Re}}$$  \hfill (10.24)

A similar insertion of the non-dimensional scaling into Eq. (10.11)c (in $y$-direction) exhibits the assertion that for $Re \gg 1$ the derivative of the pressure in $y$-direction diminishes. This means that the pressure normal to the wall does not change within the boundary layer; it is rather given by the value from the inviscid outer potential flow. The pressure $p$ in boundary layer theory is not an unknown quantity it is rather given as a boundary condition. All these order of magnitude estimates lead to the boundary layer equations, which were initially written by Ludwig Prandtl in 1904.

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 ,$$

$$\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{dp(x)}{dx} + v \frac{\partial^2 u}{\partial y^2}$$  \hfill (10.25)

These are two equations to determine the unknowns $u$, $v = f(x,y)$. Because of Bernoulli’s equation $p(x) + \rho/2u_0^2(x) = \text{const.}$ the pressure and the velocity gradient of the inviscid outer flow are coupled. The boundary conditions of the equation system are:

$$y = 0 : \quad u = v = 0 ,$$

$$y = \delta : \quad u = u_0(x)$$  \hfill (10.26)

The system of the boundary layer equations is parabolic and represents an initial boundary problem. Due to the simplification of the viscous terms diffusion processes are only active in the $y$-direction. There is no upstream flux of information and all can be calculated straight forwards downstream. This is an enormous simplification compared to the elliptic Navier-Stokes equations, for which a simultaneous solution for all domains is required. There are some exact and approximate solutions of the boundary layer equations which can be found in [Schlichting, 1979] or [Jischa, 1982].
10.4.3 Summary and comments

The main aim to treat the laminar momentum equations is to determine the local $c_L(x)$ and/or the global friction coefficient $c_W$. Many textbooks show that these values can be given in a form $c_L(x) = f(Re_x^b)$ or $c_W = f(Re_L^b)$.

Herein, $Re_\text{x}$ is the local Reynolds number and $Re_L$ the Reynolds number built with the characteristic dimension of the body. For a duct or a tube flow $n = -1$ is obtained. The friction coefficient does not change in flow direction for a fully developed flow. This is different to a boundary layer flow along a plate, because there the boundary layer thickness grows along the flow direction $x$ while the local friction coefficient decreases with $x$. In this case the local friction coefficient yields an exponent $m = -1/2$ and the total resulting friction coefficient exhibits a coefficient $n = -1/2$. Crucial in this context is that the only appearing dimensionless quantity is the Reynolds number, which can be conceived as the ratio of the inertial forces versus the viscous ones. For a fully developed flow the inertial force is replaced by the driving pressure gradient.

One can distinguish between different approaches to describe laminar flows:

- **Analytic solutions of the Navier-Stokes equations** can be only obtained for a few rather specific exceptions like the plane duct or the circular pipe flow.

- **Numeric solutions of the Navier-Stokes equations** are extremely time consuming. Here, a system of non-linear partial differential equations of the elliptic type must be solved. This is a boundary value problem and no consecutive methods like for parabolic partial differential equations can be applied. For some technically interesting cases like the developing flow into a tube or the flow near the leading edge of a plate, calculations were performed. In the engineering practice, however, these solutions are of minor importance. In the limiting case $Re \to \infty$ the Navier-Stokes equations mutate into the boundary layer equations. In many practically important cases the Reynolds number is large enough to apply the boundary layer equation. An exception in this context is the leading edge problem for which the prerequisite $\frac{d^2 \phi}{dx^2} \ll 1$ and $\frac{\partial^2 \phi}{\partial x^2} \ll \frac{\partial^2 \phi}{\partial y^2}$ is not fulfilled.

- **Exact solutions of the boundary layer equation** exist only for specific outer flows acting as boundary condition. The terminology exact means that this is not an analytic but an arbitrarily exact numeric solution of an ordinary differential equation. In case of the self-similar solutions the individual velocity profile does not alter its shape in flow direction and it can by an appropriate co-ordinate transformation reduced to the similar profile.

For an arbitrary outer flow the velocity profile changes its shape in flow direction; there exist no self-similar solutions and the boundary layer equation can only be solved numerically. This can be performed in two ways.

- **Numeric solutions of the boundary layer equations** exist for numerous cases. By means of difference methods the parabolic boundary layers equation can be numerically integrated as a initial boundary problem using a consecutive approach. Because of stability reasons implicit methods although they require more effort are preferred compared to simpler explicit schemes. The problems arising using the individual techniques are in detailed discussed in the book of Cebeci and Bradshaw (1977).

- **Integral schemes to solve the boundary layer equations** are simple to treat and practically most often used. Often used are the schemes by Pohlhausen und v. Karman. The effort required for computing time as well as the memory consumption low. Also the solution of two coupled
non-linear ordinary differential equations is not problematic. These integral methods are still
in use to calculate especially turbulent boundary layers. An exhaustive discussion on the
different types of numeric approaches may be taken in the monograph by Walz [1966].
Despite the undeniable advantages of the integral methods one crucial disadvantage exists;
the quality of the achieved results depends on the assumption of the chosen profile. The user
must know a lot of properties of the solution in order to formulate an appropriate profile.

**Empirical solutions** must be used in all cases where complex geometries do not allow a direct
numerical solution.

Finally, for completeness two problem circles should be shortly mentioned. This is the higher
order boundary layer theory. This is a perturbation theory which is called the matched asymptotic
expansions. It is a further development of Prandtl’s boundary layer concept, where the boundary layer
equation is the first order equation in the hierarchy. Effects of higher order like inclinations, etc., can
be treated in this kind of concept. An overview on the different model ideas is given in the books by
[Van Dyke, 1975] or [Cole, 1968]. The not treated rather complex issue are three-dimensional
boundary layers, which appear in many technical applications. Here, the gracious reader should refer
to the text books, e.g. [Schlichting, 1979] or [White, 1974].

### 10.5 Laminar energy exchange

In a moving fluid energy and momentum are exchanged if:

a) thermal energy is supplied to or removed from the fluid;

b) the kinetic energy of the flow is of the order of the inner energy so that by dissipation the
temperature of the fluid is increased.

In Case (a) one distinguishes between forced and free convective flows. In forced convective
flows an external forcing bean means of a supplied pressure gradient or a given outer flow is present,
while in free or natural convection flows buoyancy forces caused by density differences (which are
originating from temperature differences) are the driving source of the flow. Restricting ourselves to
steady flows of single component Newtonian fluids one obtains the energy equation in the form
described in Eq. (10.8) (see Section 10.3). The set of equations to be solved for the laminar energy
exchange reads to:

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0; \rho \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) = -\frac{\partial p}{\partial x} + \mu \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) + \rho g_x; \\
\rho \left( \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) = -\frac{\partial \rho}{\partial y} + \mu \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) + \rho g_y; \\
\rho c_p \left( \frac{\partial T}{\partial x} + \frac{\partial v}{\partial y} \right) = \lambda \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + \frac{\partial \rho}{\partial x} + \nu \frac{\partial \rho}{\partial y} + \Phi
\]

(10.27)

where the heat conductivity \( \lambda \) is assumed to be constant, \( g \) is the gravity vector in the form \( g = (g_x, g_y) \)
and \( \Phi \) is the dissipation function defined in Eq. (10.9)b.

This section deals with the laminar flow and forced convection heat transfer characteristics of a
variety of ducts interesting to heating and cooling devices in nuclear engineering. The results
presented here are applicable to straight ducts with axially unchanging cross-sections. Also the duct

---

411
walls are considered smooth, non-porous, rigid, stationary and wetted. Furthermore, the duct walls are
assumed to be uniformly thin, so that the temperature distribution within the solid walls has negligible
influence on the convective heat transfer in the flowing fluid. Thus this section covers the steady,
incompressible laminar flow of a constant property Newtonian fluid. All forms of body forces are
neglected; moreover, the effects of natural convection, phase change, mass transfer or chemical
reactions are omitted. A complete representation of the laminar heat transfer correlations and a
detailed description of the methods can be found in the monographs by [Shah and London, 1978].

10.5.1 Types of laminar duct flow

Four types of laminar duct flows exist; namely, fully developed, hydrodynamically developing,
thermally developing, and simultaneously developing. The latter means that the flow is at the same
time hydrodynamically developing and thermally developing. A brief description of these flows is
given here with an aid in Figure 10.5.1, which depicts a fluid with the uniform velocity \( u_0 \) and
temperature \( T_0 \) entering a duct of an arbitrary cross-section at \( x = 0 \).

Figure 10.5.1. Types of laminar duct flow for constant wall temperature boundary condition

(a) Hydrodynamically developing flow followed by thermally developing (and hydrodynamically developed) flow
(b) Simultaneously developing flow in liquid metals (Pr << 1)

Solid lines denote the velocity distribution while the dotted grey lines represent the temperature profiles

Referring to Figure 10.5.1, suppose that the temperature of the duct wall is kept at the entering
fluid temperature \( T_0 \) and there is no generation or dissipation of heat within the fluid. In this case the
fluid experiences no gain or loss of thermal energy. In such a case of an isothermal flow, the effect of
viscosity spreads across the ducts cross-section commencing at \( x = 0 \). The hydrodynamic boundary
layer develops according to Prandtl’s boundary layer theory (see Subsection 10.4.2) and its thickness \( \delta \)
The boundary layer separates the flow field in two domains; a viscous region near the wall and an essentially inviscid region around the ducts centreline. At \( x = l_{hy} \) the viscous effects have completely spread across the whole ducts cross-section. The domain \( 0 \leq x \leq l_{hy} \) is called the hydrodynamic entrance region and the flow in this domain is called the hydrodynamically developing flow. In the entrance region the velocity depends on all three spatial co-ordinates, while for \( x > l_{hy} \) the velocity profile is independent of the axial co-ordinate \( x \). After the flow becomes hydrodynamically developed consider that the duct wall temperature is dropped compared to the entering fluid \( T_w < T_0 \). In this case the thermal effects diffuse gradually from the duct wall commencing at \( x = l_{hy} \). The extent of the thermal diffusion is denoted by the thickness of the thermal boundary layer \( \delta_{th} \), which grows along the axial co-ordinate \( x \). A similarity analysis based on the boundary layer approximation approach immediately reveals that the thermal boundary layer grows as \( \delta_{th}(x) \sim (Re \cdot Pr)^{-1/2} \). Moreover, applying the boundary layer approach the thermal boundary layer also divides the flow field in two regions; a heat affected region close to the wall and an unaffected domain in the ducts centre. A result of the dimensional analysis is also that the ratio of the thermal boundary compared to the viscous one scales as:

\[
\frac{\delta_{th}}{\delta} = \frac{1}{\sqrt{Pr}}
\]  

At \( x = l_{th} \) the thermal effects have spread throughout the whole ducts cross-section and beyond this point the flow is called thermally developed. The region \( l_{hy} \leq x \leq l_{th} \) is termed the thermal entrance region. Here the temperature varies with all three spatial co-ordinates. The simultaneously developing flow is displayed in the lower graph of Figure 10.5.1 for a liquid metal. In this case the viscous and the thermal effects diffuse simultaneously from the duct wall towards the ducts centre commencing at \( x = 0 \). The essential parameter here is the Prandtl number, which denotes the ratio of the kinematic viscosity to thermal diffusivity. The kinematic viscosity is the diffusion rate for momentum (velocity) in the same sense that the thermal diffusivity is the diffusion rate for heat (temperature). If \( Pr = 1 \), the viscous and thermal diffuse through the fluid at the same rate. This equality of diffusion rates does not guarantee that the viscous and thermal boundary layers in close duct flows will be of the same thickness at defined axial position \( x \). The reason for this paradox lies in the fact that with \( Pr = 1 \), the applicable momentum and energy differential equations do not become analogous. As depicted in the Figure 10.5.1(b), within the region \( 0 \leq x \leq l_d \) viscous and thermal effects spread simultaneously towards the duct centre. Accordingly, this region is referred to as the combined entrance region. It is obvious that the length \( l_d \) depends on the Prandtl number. In this region both velocity and temperature depend on all three space co-ordinates. Only for \( x > l_d \) when the flow is fully developed the temperature and velocity become axially invariant and depend only on \( y \) and \( z \), i.e. \( u = u(x,y) \) and \( T = T(x,y) \).

### 10.5.2 Fluid flow and heat transfer parameters

The fluid flow characteristics of all duct flows is expressed in terms of certain hydraulic parameters. For the hydrodynamically developing flow, the dimensional axial distance \( x^+ \) is defined as:

\[
x^+ = \frac{1}{Re} \frac{x}{d_h}
\]

where \( d_h \) is the hydraulic diameter defined by \( d_h = 4A/P \) with \( A \) the ducts cross-section and \( P \) the wetted perimeter. The hydrodynamic entrance length \( l_{hy} \) is defined as the axial distance required to attain 99% of the ultimate fully developed maximum velocity when the entering flow is uniform. The dimensionless hydrodynamic entrance length is expressed by \( l_{hy}^+ = l_{hy}(d_h Re) \).
The fluid bulk mean temperature, also referred to as the “mixing cup” or flow average temperature $T_m$ is defined as:

$$T_m = \frac{1}{A u_0} \int_A T \, dA$$ (10.30)

The circumferentially averaged but axially local heat transfer coefficient $\alpha_x$ is defined by:

$$q_{w,x} = \alpha_x (T_{w,m} - T_m)$$ (10.31)

where $T_{w,m}$ is the wall mean temperature and $T_m$ is the fluid bulk mean temperature given by Eq. (10.30). The heat flux $q_w$ and the temperature difference $(T_{w,m} - T_m)$ are by nature vector quantities. In the notation (10.31) the direction of heat transfer is from the wall to the fluid, and consistently the temperature drop is from the wall to the fluid. In contrast, if $q_w$ represents the heat flux from the fluid to the wall the temperature difference entering Eq. (10.31) will be $(T_m - T_{w,m})$. The flow length averaged heat transfer coefficient $\alpha_m$ is the integrated value from $x = 0$ to $x$ in the way:

$$\alpha_m = \frac{1}{x} \int_{x=0}^{x} \alpha_x \, dx$$ (10.32)

The ratio of the convective conductance to the pure molecular conductance is defined as a Nusselt number $Nu$. The circumferentially averaged but axially local Nusselt number $Nux$ is defined as:

$$Nux = \frac{\alpha_x \, d_h}{\lambda} = \frac{q_{w,x} \, d_h}{\lambda (T_{w,m} - T_m)}$$ (10.33)

Thus the Nusselt number is nothing else than the dimensionless temperature gradient at the wall. The Nusselt number can also be conceived as a ratio of two different lengths, namely the ratio of the characteristic length to the local thickness of the thermal boundary layer. The mean Nusselt number $Nutm$ based on $\alpha_m$ in the thermal entrance region reads to:

$$Nutm = \frac{1}{x} \int_{x=0}^{x} Nux \, dx = \frac{\alpha_m \, d_h}{\lambda} = \frac{q_{w,m} \, d_h}{\lambda (\Delta T)_m}$$ (10.34)

The expression for $(\Delta T)_m$ could become complicated and depend upon the thermal boundary conditions. The dimensionless axial distance $x^*$ is defined as:

$$x^* = \frac{1}{Pe} \frac{x}{d_h} = \frac{1}{RePr} \frac{x}{d_h}$$ (10.35)

The thermal entrance length $l_{th}$ is defined as the axial distance required to achieve a value of the local Nusselt number $Nut$, which is 1.05 times the fully developed Nusselt number value. The dimensionless thermal entrance length is expressed as $l_{th}^* = l_{th} / (d_h Pe)$.

Also often the Stanton number $St$ is used. It describes the ratio of the heat flux transferred from the wall to the enthalpy difference of the outer flow and is defined as:

$$St = \frac{\alpha}{\rho c_p u_0} = \frac{q_w}{\rho c_p u_0 (\Delta T)} = \frac{Nu}{RePr}$$ (10.36)
10.5.3 Thermal boundary conditions

In order accurately interpret the highly sophisticated heat transfer results in the ensuing sections, a clear understanding of the thermal boundary conditions imposed on the duct walls is absolutely essential. A systematic exposition of the boundary conditions is provided by [Shah and London, 1978]. Here we focus on the technically most important ones.

a) Uniform wall temperature \( T_w \) with circumferentially and axially constant wall temperature, which is expressed by Eq. (10.37). It appears mostly in condensers or evaporators.

\[
T_w = \text{const.} \quad (10.37)
\]

b) Convective with axially constant wall temperature and finite thermal resistance normal to the wall. It is in principle the same as a) except that the wall thermal resistance is finite in these applications, which can yield to an upstream heating of the fluid. Especially in liquid metal heat transfer experiments this condition mostly appears, because they can not be directly heated due to their good electric conductivity. The formulation of this boundary condition reads to:

\[
\begin{align*}
T_{w0} &= T_w (y, z); T_w = T_w (x, y, z);
\lambda \frac{\partial T}{\partial n} &= \alpha_0 (T_{w0} - T_w);
\frac{1}{\alpha_0} &= \frac{t_w}{\lambda_w} + \frac{1}{\alpha_e}
\end{align*}
\]

where \( T_{w0} \) is the temperature at the outside of the heater/cooler, \( T_w \) the fluid/wall interface temperature, \( \alpha_0 \) the heat transfer coefficient at the fluid/wall interface, \( \lambda_w \) the heat conductivity of the wall, \( t_w \) its thickness, \( n \) the wall normal unity vector and \( \alpha_e \) the heat transfer coefficient at the entrance, where the heat transfer starts.

c) Constant wall heat flux with circumferentially constant wall temperature and axially constant wall heat flux. This condition applies for electric resistance heating, nuclear heating and heat exchangers having nearly identical fluid capacity rates. However, this condition only applies if the wall materials are thermally highly conducting, i.e. \( \lambda_w \gg \lambda \) or the wall is considerably thinner than the characteristic duct dimensions. This condition is formulated by:

\[
q_w = q_w (y, z); T_w = T_w (x) \quad (10.39)
\]

d) Uniform axial and circumferential heat flux, which is nearly the same condition as for case c), but it refers to boundary conditions where the wall material has a low thermal conductivity and the wall thickness is uniform. It reads to:

\[
q_w = \text{const.} \quad (10.40)
\]

e) Convective with axially constant wall heat flux and a finite thermal resistance normal to the wall. Also this condition is nearly the same as case c) except for the finite thermal resistance normal to the wall. Moreover, there is assumed that there is negligible heat conduction along the ducts circumference. This condition is expressed by:

\[
q_w = q_w (y, z); \lambda \frac{\partial T}{\partial n} = \alpha_0 (T_{w0} - T_w) \quad (10.41)
\]
f) Finally, the conductive boundary condition with axially constant wall heat flux and finite heat
conduction along the walls circumference, which is an extension of the case e). This boundary
condition is described by:

\[
q_w = q_w(y, z) = \frac{\partial T}{\partial n} + \frac{\lambda_w T_w}{\lambda} \frac{\partial^2 T}{\partial s^2} = 0
\]

(10.42)

where \( s \) is the circumferential co-ordinate.

This list of boundary conditions applies both for the laminar and the turbulent heat transfer
phenomena and it demonstrates the necessity for a detailed description of the experimental set-up.
Only a complete description of the thermo-physical properties of the materials used, the heater type
applied and the exact geometric dimensions allows to judge on the thermal boundary condition to be
applied for the analysis of the experiment. Apart from the choice of the correct boundary conditions it
says nothing about the quality of the performance of the experiment. Even a laminar experiment may
be superimposed by buoyancy effects which considerably changes the experimental results.

10.5.4 Laminar heat transfer in circular ducts

The circular duct is the most widely used geometry in fluid flow and heat transfer devices.
Accordingly, it has been analysed in detail for various boundary conditions. Also available in literature
is a lot of information on the effects of viscous dissipation, fluid axial conduction, thermal energy
sources and axial momentum diffusion. Some of the results will be shown within this subsection.

10.5.4.1 Fully developed flow

The velocity profile and the leading correlations for a fully developed laminar flow in a circular
duct are elaborated already in Subsection 10.4.2. In this context we refer to these equations and show
the results for the different thermal boundary conditions.

a) Uniform wall temperature (condition a)

The temperature distribution in circular ducts for non-dissipative flows in the absence of flow
work, thermal energy sources and fluid axial conduction is given exactly. The expression for the fluid
bulk mean temperature is given by the following asymptotic formula applicable for \( x^* > 0.0335 \), see
[Bhatti, 1985]:

\[
\frac{T_w - T_m}{T_w - T_r} = 0.819048 \exp(-2\lambda_0^2 x^*) \quad \text{with} \quad \lambda_0 = 2.70436442
\]

(10.43)

It should be noted that although the local temperature \( T \) is both a function of the radial and the
axial co-ordinates the fluid mean bulk temperature \( T_m \) depends on the axial co-ordinate only (the
dimensionless temperature \( (T_w - T)/(T_w - T_m) \) is only a function of the radius. The Nusselt number of
the fully developed flow can be calculated to:

\[
Nu = \frac{\lambda_0^2}{2} = 3.6568
\]

(10.44)
For fully developed flows and the thermal condition a) is the result is independent of the Prandtl number of the fluid. However, if the Peclet number $Pe$ is smaller than 10, the influence of the axial fluid conduction is not negligible anymore. In this parameter regime the asymptotic expressions presented by [Michelsen and Villadsen, 1974] are recommended:

\[
Nu = \begin{cases} 
4.180654 - 0.18346 \cdot Pe & \text{for } Pe < 1.5 \\
3.656794 + 4.4870 / Pe^2 & \text{for } Pe > 5.0 
\end{cases}
\] (10.45)

b) Uniform wall heat flux ($q_w = \text{const. condition } d$)

The temperature distribution in circular ducts for non-dissipative flows in the absence of flow work, thermal energy sources and fluid axial conduction can be written analytically in the following form:

\[
\frac{T_w - T}{T_w - T_m} = 6 \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \left[ 3 - \left( \frac{r}{R} \right)^2 \right] ; \quad \lambda \left( \frac{T_w - T_m}{q_w d_h} \right) = \frac{11}{48} = \frac{1}{\lambda} = \frac{\lambda}{\alpha d_h}
\] (10.46)

The Nusselt number obtained for constant wall heat flux is for a fully developed laminar flow about 20% larger than that for constant wall heat flux. The qualitative shape of the fluid bulk mean temperature distribution the wall heat flux and the wall temperature profile as a function of the axial co-ordinate $x$ is qualitatively depicted in Figure 10.5.2.

**Figure 10.5.2.** Qualitative shape of the fluid bulk mean temperature, the wall temperature and the wall heat flux for the case of a constant wall heat flux $q_w = \text{const.}$ (condition d) left graph and a constant wall temperature $T_w = \text{const}$ (condition a) right graph

c) Convectively heated or cooled duct wall (condition b)

For this boundary condition the temperature is assumed to be constant axially but the duct has a finite thermal resistance normal to the wall. The thermal resistance can be embedded in an external convective heat transfer coefficient $\alpha_c$, which is included in the dimensionless Biot number $Bi$ defined as $Bi = \alpha_c d / \lambda_c$. The Biot number can also include the effect of the wall thermal resistance. In this case $Bi = 1 / R_w$, where $R_w = (\lambda_c / \alpha_c d) + (\lambda_c / \alpha_c d_c)$. The limiting cases are the constant wall temperature condition corresponding to $Bi \to \infty$ and the constant heat flux condition implying $Bi = 0$. Hence the Biot number can be conceived as a ratio of the thermal resistance of the wall compared to that of the fluid. For a constant $\alpha_c$ [Hickman, 1974] developed an asymptotic solution for the Nusselt number in the form (10.47). The overall mean Nusselt number $Nu_{o,m}$ then reads to:
$$Nu = \frac{\frac{48}{11} + Bi}{1 + \frac{59}{220} Bi} ; \quad \frac{1}{Nu_{o,m}} = \frac{1}{Nu} + \frac{1}{Bi}$$

$$Nu_{o,m} = \frac{\alpha_o d_h}{\lambda} = \frac{q_o d_h}{\lambda(T - T_m)}$$ (10.47)

$Nu_{o,m}$ is quite insensitive to circumferential variation of $Bi$ according to [Sparrow, et al., 1978].

### 10.5.4.2 Hydrodynamically developing flow

The problem of hydrodynamic flow development has been theoretically investigated by numerous scientists. Depending on the Reynolds numbers various solutions can be categorised as:

- a) solutions involving the boundary layer equations valid for Reynolds number $Re > 400$;
- b) solutions involving the Navier-Stokes equations for $Re < 400$;
- c) creeping flow solution for $Re \rightarrow 0$, which hardly exist in liquid metal flows.

#### a) Solutions involving the boundary layer simplification

The various solutions using this approach are reviewed and classified in detail by the book of [Shah and London, 1978]. Among them the numerical solution of [Hornbeck, 1964] is technically most used. According to these results the dimensionless hydraulic developing length $l_{hy}$ and the dimensionless pressure gradient $\Delta p^*$ can be calculated using:

$$l_{hy} = 0.0565 ; \quad \Delta p^* = 13.74 \sqrt{x^*} + \frac{12.5 \times 64 x^* - 13.74 \sqrt{x^*}}{1 + 2.1 \times 10^{-4} (x^*)^2}$$ (10.48)

#### b) Solutions involving the Navier-Stokes equations

Close to the duct inlet the axial momentum diffusion and the radial pressure variation are of importance. The proper accounting of these effects introduces the Reynolds number as a parameter in the solution and also requires a careful specification of the inlet flow velocity profile. Using modern computational fluid dynamic code packages this problem can be arbitrarily exact solved for different inlet velocity distributions. Assuming a constant velocity far of the inlet the analysis by [Chen, 1973] can be used as most accurate for the hydraulic developing length. It reads to:

$$l_{hy}^* = 0.056 + \frac{0.6}{Re(1 + 0.035 Re)}$$ (10.49)

### 10.5.4.3 Thermally developing flow

Within this subsection a hydrodynamically fully developed flow is assumed for the velocity distribution in the circular duct. The temperature profile is allowed to develop under the individual thermal boundary conditions.

#### a) Constant wall temperature ($T_w = \text{const}$.)

Neglecting viscous dissipation, fluid axial conduction and thermal energy sources the solution of the problem is called in the literature the Graetz problem [Graetz, 1885], who solved this configuration...
analytically. Based on the Graetz and extended Leveque solutions, the local Nusselt number $N_u$ can be obtained from the following formulas depending on the axial co-ordinate $x^*$:

\[
N_u = \begin{cases} 
1.077(x^*)^{1/3} - 0.7 & \text{for } x^* \leq 0.1 \\
3.657 + 6.874(10^3x^*)^{-0.468}\exp(-57.2x^*) & \text{for } x^* \geq 0.1
\end{cases}
\] (10.50)

[Hausen, 1943] presented the following correlation for the mean Nusselt number $N_{u_m}$ valid in the entire range of $x^*$:

\[
N_{u_m} = 3.66 + \frac{0.0668}{x^{1/3}(0.04 + x^{2/3})}
\] (10.51)

The error is in the range of 2% compared to a full numerical solution. The effect of fluid axial conduction is negligible for $Pe > 50$, according to [Hennecke, 1968]. However, the thermal developing length $l_{th}$ increases considerably from 0.033 for $Pe = \infty$ to 0.5 for $Pe = 1$. The dimensionless temperature distribution $T^*$ as a function of $r/R$ and $x^*$ is depicted in Figure 10.5.3(a) and the mean local Nusselt number $N_u$ and the mean Nusselt number $N_{u_m}$ is shown in Figure 10.5.4(a).

\(b)\) **Constant wall heat flux ($q_w = \text{const.}$)**

Similar to the Graetz problem with $T_w = \text{constant}$ solution, the thermal entrance length for the thermally developing flow with $q_w = \text{const.}$ is of large practical interest. The solution obtained for this problem can be analytically expressed in terms of a series as demonstrated by [Siegel, et al., 1958] or [Hsu, 1965]. Based on the Graetz type and Leveque solutions also the mean local Nusselt number $N_u$ and the mean Nusselt number $N_{u_m}$ can be expressed by approximation formulas, which where derived by [Bird, et al., 1960].

\[
N_u = \begin{cases} 
1.302(x^*)^{1/3} - 1.0 & \text{for } x^* \leq 5 \cdot 10^{-4} \\
1.302(x^*)^{1/3} - 0.5 & \text{for } 5 \cdot 10^{-3} \leq x^* \leq 1.5 \cdot 10^{-4} \\
4.364 + 8.68(10^3x^*)^{-0.56}\exp(-41x^*) & \text{for } x^* \geq 1.5 \cdot 10^{-3}
\end{cases}
\] (10.52)

\[
N_{u_m} = \begin{cases} 
1.953(x^*)^{1/3} & \text{for } x^* \leq 0.03 \\
4.364 + 0.0722/x^* & \text{for } x^* \geq 0.03
\end{cases}
\] (10.53)

The error made by the approximation is about $\pm 2\%$ compared to the exact solution. From the analysis of [Hennecke, 1968] the effect of fluid axial conduction is negligible for $Pe > 10$ if $x^* > 0.005$, which is less than for constant wall temperature. The thermal entrance or developing length $l_{th}$ is found to be 0.0430527, see [Grigull and Tratz, 1965].

\(c)\) **Convectively heated or cooled duct wall (condition b in Section 10.5.2)**

The convective boundary condition can also be solved by means of a series expansion incorporating the Biot number, see [Hsu, 1968]. The local Nusselt numbers as a function of the dimensionless distance $x^*$ for different Biot numbers are shown in Figure 10.5.4(b). The curves corresponding to $BI = 0$ ($q_w = \text{const.}$) and $BI \to \infty$ ($T_w = \text{const.}$) are the same as in Figure 10.5.4(a).
Figure 10.5.3. Dimensionless temperature distribution in the thermal entrance region of a circular duct and a thermally developing laminar flow as a function of the dimensionless length $x^*$ for the thermal condition $T_\psi = \text{constant}$ (a) and the condition $q_w = \text{constant}$ (b) from [Grigull and Tratz, 1965]

$$T = \left( T_w - T_e \right) T = 8/79 \left( T_w - T_e \right) 3 \left( q_w d \right)^{0.8}$$

![Temperature Distribution Diagram](image1)

Figure 10.5.4. Nusselt number as a function of the dimensionless entrance length $x^*$ for a hydraulically developed and thermally developing laminar flow in a circular tube

a) Local and mean Nusselt numbers $N_{ux}$ and $N_{um}$ for $T_w = \text{constant}$ and $q_w = \text{constant}$

b) Local Nusselt number $N_{ux}$ for mixed convective thermal boundary conditions expressed by the Biot number

![Nusselt Number Diagram](image2)

10.5.4.4 Simultaneously developing flow

All results presented so far have been based on the rather idealised assumption of an already hydraulically fully developed flow. This assumption is in most cases far away from the practical use in liquid metals, because in flows with the Prandtl number being far below unity, the hydraulic entrance length is considerably longer than the thermal one (see discussion in Section 10.5.1). The idealisation of a fully developed velocity profile at the duct inlet may lead to a significant error in the predicted performance. In such cases, the results pertaining to simultaneously developing velocity and temperature profiles should be applied. An inherent result of the both flow types developing is that the solution depends immediately on the Prandtl number. Subsequent we discuss the results for a circular duct for different thermal boundary conditions.
a) Uniform wall temperature \((T_w = \text{const.})\)

For \(Pr \rightarrow \infty\) the flow is hydraulically already developed before the temperature profile starts developing. This represents the limiting case discussed in Subsection 10.5.3.3. According the Nussel numbers curves coincide. In case of a good conducting fluid, assume idealised that \(Pr = 0\) the temperature profile develops much faster than the velocity profile. So in this limiting case, while the temperature profile develops the velocity distribution remains nearly unchanged. The non-modified velocity profile with its small boundary layer has a large flow rate close to the wall, which immediately yields considerably larger heat transfer from the wall expressed by the Nusselt number. The solution for the limiting cases were already obtained by [Graetz, 1883] and rediscovered by [Leveque, 1928]. For the ideal case of \(Pr = 0\) and \(Pr \rightarrow \infty\) the solutions can be expressed by analytic means, while for the other Prandtl number series expansions incorporating Bessel functions and numerical approximations are necessary. The mean and the local Nusselt numbers \(Nu_x\) and \(Nu_m\) as a function of the dimensionless entrance length \(x^*\) for different Prandtl numbers are displayed in Figures 10.5.5(a) and (b).

**Figure 10.5.5. Local and mean Nusselt numbers \(Nu_x\) (a) and \(Nu_m\) (b) as a function of the dimensionless entrance length \(x^*\) for a simultaneously developing flow in a circular tube with the thermal boundary condition \(T_w = \text{constant}\) and for different fluids expressed by the Prandtl number**

![Figure showing local and mean Nusselt numbers](image)

Note that for \(Pr = 0\) the local and the mean Nusselt number approach the value of 5.7832, whereas the remainder of the curves approach the value of 3.6568. The thermal entrance lengths for the simultaneously developing are according to [Bhatti, 1985] found to be:

\[
I_{th}^* = \begin{cases} 
0.028 & \text{for } Pr = 0 \\
0.037 & \text{for } Pr = 0.7 \\
0.033 & \text{for } Pr \rightarrow \infty 
\end{cases}
\]  

(10.54)

b) Uniform wall heat flux \((q_w = \text{const.})\)

A similar approach like for the previous thermal boundary condition can be used for the case with a uniform wall heat flux. It is interesting to note, that the curve for the local Nusselt number in case of \(Pr = 0\) tends for large \(x^*\) to the asymptotic value of 8, which is about 40% more than for the uniform wall temperature condition. The dependence of the local Nusselt number as a function of the entrance length is shown in Figure 10.5.6. Not only the heat transfer is larger in for the uniform wall heat flux
but also the thermal entrance length increases. In case of well molecular conducting fluids it is by 50% larger than for the uniform wall temperature. The analysis performed by [Bhatti, 1985b] yields the following values:

$$I_{th}^* = \begin{cases} \frac{0.042}{Pr} & \text{for } Pr = 0 \\ \frac{0.053}{Pr} & \text{for } Pr = 0.7 \\ 0.043 & \text{for } Pr \to \infty \end{cases}$$ \hspace{1cm} (10.55)

**Figure 10.5.6.** Local Nusselt numbers $Nu_x$ as a function of the dimensionless entrance length $x^*$ for a simultaneously developing flow in a circular tube with the thermal boundary condition $q_w = \text{constant}$ and for different fluids.

### 10.5.5 Summary on the laminar heat transfer

Within this section the laminar heat transfer has been considered for different thermal boundary conditions. The description has been focused to describe the main effects of developing length, heat local and global transfer performance under different thermal boundary conditions. The effect of the fluid properties in the non-dimensional sense were found to play a crucial role for developing flows. This section was intended to define the terminology of the individual transport properties, which will be kept the same throughout this chapter on thermal-hydraulics.

The central task of this laminar heat transfer section was to determine the wall heat flux transferred at the fluid wall interface in dependence on the specific geometries (here mainly the circular duct) and on the fluid properties. More details on the heat transfer in other geometries may be taken from [Shah and London, 1985]. The wall heat flux is given by $q_w = -\lambda(\partial T/\partial n)_w$, and it depends only on the molecular heat conductivity of the individual fluid and the temperature gradient at the wall.

Although the laminar heat transfer is a pure molecular transport process the flow field plays an essential role. For the convective transport of internal energy or enthalpy the flow is responsible and influences the temperature gradient in a significant manner. It is obvious that the heat transfer can be enhanced by increasing the flow velocity. The faster energy is convectively transported the more energy can be removed from the wall. For incompressible fluids the flow field is determined by only one characteristic number. In forced convective problems this is the Reynolds number, while in buoyant convection the Grashof number appears. In both characteristic numbers the molecular viscosity $\nu$ appear, which is responsible for the momentum exchange. For the heat exchange in a
flowing liquid the ratio of the molecular viscosity $\nu$ to the molecular heat conductance $\kappa = \lambda/(\rho c_p)$, the so-called Prandtl number, is of crucial importance. In contrast to the Reynolds or the Grashof number the Prandtl number is a pure material constant and it depends only on the fluid properties.

One normalises the wall heat flux with an appropriate temperature difference and this is named the heat transfer coefficient $\alpha = q_w/\Delta T$. The heat transfer coefficient can be represented non-dimensional in different manners. The Stanton number is the ratio of the wall heat flux to the enthalpy difference density and does not contain the heat conductivity. More often used is the Nusselt number, in which the heat transfer coefficient multiplied with a characteristic dimension is related to the molecular heat conductivity. In case of pure forced convection the results can be compressed in the way:

$$\frac{Nu_x}{\sqrt{Re_x}} = f(Pr^n) \text{ with } 0 < n < 1$$

The expression $Nu_x/\sqrt{Re_x}$ increases with rising Prandtl number. This does not mean that the heat transfer or the heat transfer coefficient also increases with increasing Prandtl number, because the Nusselt number itself contains the molecular heat conductivity.

For a fully developed flow (both thermally and hydrodynamically) the heat transfer is given only by a constant Nusselt number. The constants depend uniquely on the chosen thermal boundary condition. The Prandtl number influences only the heat transfer in the thermal entrance (or developing) region.

In order to determine the heat transfer correlation there exist in principle the following possibilities:

- Analytic solutions including the whole set of conservation equations. Mostly, this is only applicable for drastic simplifications like the fully developed duct flow or the Couette-flow.
- Numeric solution of the conservation equations. This requires a lot of effort in computing time and memory capacity, since the equations are of elliptic type. However, the progress of the computers in calculation power makes many problems even now tractable.
- Exact solutions of the boundary layer equations. The similar solutions are of major importance for the determination of heat transfer correlations, since they are available in tables, diagrams or in form of series approximations.
- Numeric solutions of the boundary layer equations require mathematical effort, but are with commercially available computational fluid dynamics codes easier accessible than in the past.
- Approximate solutions using integral methods. They are less accurate than numeric solutions but they are still in practical use. The numeric effort is low and complex and expensive codes are not necessary.
- Analogies between heat and momentum transfer are only applicable for $Pr = 1$ fluids and are results of exact solutions.
- Empirical correlations. They must be used if complex geometries do not allow another solution.

### 10.6 Turbulent momentum exchange

Turbulent flows are of immense technological importance for all liquid metal applications as they occur normally under usual operation conditions. The main advantage of turbulent flows over laminar flows is that they are capable of providing vastly enhanced heat and mass transfer rates. However this is at the expense of increased friction factors accompanying the turbulent flows.
The fluid flow and heat transfer characteristics of all ducts are described in terms of certain hydrodynamic and thermal parameters. Many of them have been explained in the sections of the laminar momentum and energy exchange. In order to describe turbulent flows additional parameters that are peculiar to turbulent duct flows will be defined.

10.6.1 Description of turbulence

In the year 1883 Osborne Reynolds showed with his famous colour stripe water experiment that a laminar tube flow above a certain flow rate turns into a turbulent flow. This critical threshold or border for the transition is given by a critical Reynolds number. He found in the experiments that the transition occurs at $Re_{crit} \approx 2.300$ and supposed that the laminar-turbulent transition is a stability problem. For the development of turbulence mainly two questions are of importance:

- How develops turbulence from a laminar flow? This is essentially the stability problem of the laminar turbulent transition, which has been initially solved by Tollmien 1929 by means of a perturbation analysis. A detailed description of the methodology, the assumptions used and the interpretation of the obtained results for this type of analysis is far beyond this chapter. Here, a extensive amount of literature exists. As examples the books of [Schlichting, 1979], [Lin, 1961], [Betchov and Criminale, 1967] and [White, 1974] are recommended for the interested reader.

- How emerges turbulence in an already turbulent flow? Why remains a turbulent flow turbulent? This is mainly a question of the production of turbulence.

Turbulent flows are always unsteady, three-dimensional and stochastic. From experiments it is known that the laminar turbulent transition is accompanied by:

- an increase of the pressure drop;
- an increase of the boundary layer thickness.

This is caused by turbulent diffusion. Due to the intense macroscopic oscillation motion the turbulent velocity profile becomes “fuller” and the turbulent boundary layer gets thicker than in the laminar case. All variables in the turbulent flow depend on the spatial co-ordinates $x$, $y$ and $z$ and the time $t$. Restricting the considerations to incompressible single component flows the unknowns of the isothermal flow are $u$, $v$, $w$ and $p$ which are all functions of the three space co-ordinates and the time. Consider a in the mean steady flow, which means that it is statistically steady, then the flow variables can be decomposed in a time averaged mean value plus the fluctuations around the mean value. For the velocity this so-called Reynolds decomposition reads to:

$$u_i(x_i, t) = \overline{u_i(x_i)} + u_i'(x_i, t)$$

where we have used the tensorial notation in the form $u_i = (u, v, w)$. The time averaged mean is given by:

$$\overline{u_i(x_i)} = \frac{1}{\Delta t} \int_{x_i}^{x_i+\Delta x} u_i(x_i, t) dt$$

where the time interval $\Delta t$, over which is integrated, must be sufficiently large but not too large to retain the capability to study long term unsteady changes of the flow. By definition the time average of the fluctuations diminishes, but the mean value of their squares is far from being zero. The turbulence intensity or $RMS$ value is given by:
\[ \phi = \sqrt{u'^2} = \sqrt{u^2 + v^2 + w^2} \]  
(10.59)

The relative intensity of the velocity fluctuations is defined:

\[ T_u = \frac{\sqrt{u'^2}}{u} \]  
(10.60)

is called the turbulence level. According to [Jischa, 1982] the turbulence level is about 1% downstream a sieve, approximately 10% close to a wall and more than 10% in a free jet. Generally, the turbulent flow types can be divided in three classes:

- **Isotropic turbulence**: The statistic properties in the whole flow field are the same and are independent of the direction \((u^2 = v^2 = w^2)\). They are invariant against any translation and rotation of the co-ordinate system.

- **Homogeneous turbulence**: All statistic properties depend only on the direction and not on the location. They are translation invariant.

- **Anisotropic or shear turbulence**: This is of practical interest in technical applications, since it appears in boundary layer flows, free jets, duct flows, etc.

### 10.6.2 Reynolds equations for turbulent flows and derivation of transport equations

The unsteady Navier-Stokes equations are generally considered to be valid for turbulent flows in the continuum regime. However, the complexity and random nature of the turbulent motion prevents an exact solution of these equations. Most of the present day prediction methods for turbulent flows are based on the time averaged Navier-Stokes equations. These equations are referred to as the Reynolds equations. Time averaging the equation of motion gives rise to new terms which can be interpreted as apparent stress gradients or heat flux quantities associated with the turbulent motion. These new quantities must be related to the mean flow variables through turbulence models. This transfer process introduces further assumptions and approximations. Thus, this attack on the turbulent flow problem through solving the Reynolds equations of motion does not follow entirely from first principles, since additional assumptions must be made to “close” the system of equations. In the subsequent listing of the Reynolds equations, one in the mean steady flow of an incompressible Newtonian fluid is considered.

- **Reynolds form of the continuity equation**:

\[ \frac{\partial \overline{u_i}}{\partial x_i} = 0 = \frac{\partial \overline{u}}{\partial x} + \frac{\partial \overline{v}}{\partial y} + \frac{\partial \overline{w}}{\partial z} \]  
(10.61)

- **Reynolds form of the momentum equation**:

\[ \rho \overline{u_i} \frac{\partial \overline{u_i}}{\partial x_i} = -\frac{\partial \overline{p}}{\partial x_i} + \frac{\partial}{\partial x_j} \left( \frac{\mu}{\partial x_j} \overline{\mu_i u_j} - \rho \overline{u_i u_j} \right) \]  
(10.62)

Here appears the apparent or virtual Reynolds stress tensor \( \tau_{ij} = -\rho \overline{u_i u_j} \) which differs from the molecular one which is given by \( \tau_{ij} = \mu \left( \frac{\partial \overline{u_i}}{\partial x_j} + \frac{\partial \overline{u_i}}{\partial x_j} \right) \). It is important to note that the additional Reynolds stresses are only registered in relation to the temporal mean motion. The equation of motion
The starting point for the formulation of the transport equations is the derivation of the Navier-Stokes equation for the instantaneous quantities. Following a strict mathematical derivation process according to [Rotta, 1972] the transport equations for the Reynolds stress tensor is obtained:

\[
\frac{\partial}{\partial t} \left( \frac{v_i}{c} \frac{\partial \overline{v_i v_j}}{\partial x_k} \right) + \frac{\partial v_j}{\partial x_k} \frac{\partial \overline{v_i v_j}}{\partial x_k} + v_j v_i \frac{\partial \overline{v_i v_j}}{\partial x_k} + 2v \frac{\partial \overline{v_i v_j}}{\partial x_i} \frac{\partial \overline{v_i v_j}}{\partial x_k} - \frac{p'}{\rho} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) = 0
\]

Herein \( C \) is the convective change and \( P \) the turbulence production, which is the product of the Reynolds stress tensor with the velocity gradients of the time averaged mean velocity. \( DS \) represents the turbulent dissipation, which is essentially a negative production, \( PSC \) is pressure shear correlation, which contributes similar like the diffusion \( D \) to the reorganisation of the flow. The production term is the most essential one, since it describes that only in flows with a velocity gradient (shear flows) turbulence can be maintained. The velocity gradient of the time averaged velocity is the generator of turbulence. The necessary energy is taken from the mean flow. The tensor equation exists of nine components. An important case of the transport equation is obtained by the formal contraction \( i = j \), for which the transport equation of the turbulent kinetic energy \( k \) is obtained. If one defines \( k \) as \( k = 1/2 \overline{v_j^2} = 1/2(\overline{u^2} + \overline{v^2} + \overline{w^2}) \) the transport equation for the turbulent energy reads to:

\[
\frac{\partial k}{\partial t} \frac{v_k}{c} \frac{\partial \overline{v_i v_j}}{\partial x_k} + v_j v_i \frac{\partial \overline{v_i v_j}}{\partial x_k} + \frac{\partial}{\partial x_k} \left[ \frac{k + \frac{p'}{\rho}}{\rho} \left( \frac{\partial v_i}{\partial x_k} - v \frac{\partial v_i}{\partial x_j} \right) \right] = 0
\]

in which \( \varepsilon \) is the dissipation. The turbulence energy is not averaged and the turbulent dissipation \( \varepsilon \) is given by:

\[
\varepsilon = - \frac{\partial v_i}{\partial x_k} \left( \frac{\partial v_j}{\partial x_k} + \frac{\partial v_k}{\partial x_j} \right)
\]

The transport equations play an essential role in the development of modern turbulent flow calculation methods. Although the Reynolds stress tensor can be described by the transport equations, these equations does not solve the closure problem, since they contain unknown correlation functions. For the correlation functions new transport equations can be formulated, which themselves contain new unknown correlations. The order of the obtained tensors increases with each step by the factor one.
To summarise, the closure problem cannot be solved directly. There exist always more unknowns than the available equations. The only closure possibility is the use of semi-empirical closure assumptions, which in the simplest form can be applied directly to the Reynolds equations like the Prandtl mixing length model.

### 10.6.3 A flashlight on turbulence modelling

Several attempts have been made to solve the turbulence closure problem by the introduction of a succession of turbulence models. The simplest one of them is Prandtl’s mixing length model, see [Prandtl, 1928]. This model and its variations on the hand of [Taylor, 1915], [v. Karman, 1931] and [Van Driest, 1956] have proven reasonably adequate for plain two-dimensional flows.

For the general case of three-dimensional flows higher order turbulence models are required. They utilise one or more partial differential equations derived from the modified Navier-Stokes equations for quantities like the turbulent kinetic energy $k$, the kinetic energy dissipation $\varepsilon$, and the components of the turbulent stress tensor $\tau_{ij}$.

The turbulence model employing the single partial differential equation for the turbulent kinetic energy in conjunction with the algebraic expression for the turbulence length scale (e.g. Prandtl mixing length $l$) is referred to as the one equation model or $k-l$-model.

Another model, employing the partial differential equations for the kinetic energy and its dissipation is called the two-equation $k-\varepsilon$ model, which has been initially proposed by [Harlow and Nakayama, 1968] and modified by [Jones and Launder, 1972] and [Launder and Spalding, 1974]. It is technically most often used and spread nearly throughout all commercially available codes. Many applications of the $k-\varepsilon$ model have made use of wall functions to treat the near wall region. Alternatively, additional terms have been added to the $k$ and $\varepsilon$ to extend their applicability to the viscous sublayer by [Jones and Launder, 1972] or [Chien, 1982]. In this connection the viscous sublayer is often referred to as the region of low turbulence Reynolds number ($k^{1/2}/l/\nu$). The inner model is crucial for complex turbulent flows as for example those containing flow separation or severe property variations. The uncertainty of such inner-region modelling for complex flows appears to limit the range of the applicability of the $k-\varepsilon$ model. The $k-\varepsilon$ models that have been modified so that they are applicable in the viscous sublayer [Jones and Launder, 1972 or Rodi, 1980] are known as low Reynolds number $k-\varepsilon$ models. Details of such models are beyond the aim of this article. Modifications to the $k-\varepsilon$ model to include the effect of buoyancy and streamline curvature on the turbulence structure have also been proposed. Numerous other two-equation models have been suggested, the most frequently used being the Ng-Spalding [Ng-Spalding, 1972] model, and the [Wilcox and Traci, 1976] model. All of these models employ a modelled form of the turbulence kinetic energy equation, but the modelling for the gradient diffusion term is different. The most striking difference, however, is in the choice of dependent variable for the second model transport equation from which the length scale is determined. Often two-equation models coexist; a famous example is the so-called shear stress turbulence model (SST). The SST model combines the advantages of the $k-\varepsilon$ model with the ones of the $k-\omega$ model, where $\omega$ is the vorticity. It takes advantage of the fact that for using in the near wall region the $k-\omega$ model an analytical solution for the viscous sublayer is known for small $y^+$ values, see e.g. [Wilcox, 1986]. The matching of the $k-\omega$ model close to all walls to the $k-\varepsilon$ model in the rest of the fluid domain is performed by means of blending functions.

The complicated multi-equation models involve solutions of the partial differential equations for all components of the turbulent stress tensor and are referred to as stress equation models. A brief description of the turbulence models together with pertinent references is amongst the tremendous
literature available in this field given in the articles and books by [Reynolds, 1976] and [Arpaci and Larsen, 1984]. Here only the main ideas of these Reynolds stress models (RSM) are outlined. RSM models are those models that do not assume that the turbulent shearing stress is proportional to the rate of strain. That is for a 2-D incompressible flow:

\[-\rho u \overline{v} \neq \mu_t \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)\]  

(10.66)

in which \(\mu_t\) is the turbulent viscosity being \(\mu_t = k^2/\varepsilon\). The most widely used Reynolds stress models are those of [Hanjalic and Launder, 1972], [Launder et al., 1975] and [Donaldson, 1972]. The RSM require at least three additional partial differential equations (PDE) compared to the \(k-\varepsilon\) model and the RSM must still utilise approximations and assumptions in modelling terms which presently are difficult to measure experimentally. A simplification of the Reynolds stress modelling known as an algebraic stress or flux model has a large popularity in isothermal flows. This approach is discussed in detail in [Rodi, 1981]. In the algebraic stress modelling it is generally assumed that the transport of the Reynolds stresses is proportional to the transport of the turbulent kinetic energy. For boundary layer flows without buoyancy effects, the algebraic stress model results in:

\[\overline{u'v'} = C_\mu \frac{k^2}{\varepsilon} \frac{\partial u}{\partial y}\]  

(10.67)

which is identical to the results obtained from the \(k-\varepsilon\) model. However, in the algebraic stress model, \(C_\mu\) becomes a function of the ratio of the production to dissipation of the turbulent kinetic energy rather than a constant.

10.6.4 Boundary layer approximations

Many technical flows have boundary layer character. The laminar boundary layer equations as derived in Section 10.4.2 can not be transferred to the turbulent case because the oscillation velocities \(v_i\) are rapid in space and time and so their derivatives are not negligible compared to the other terms, although their absolute magnitude is an order of magnitude smaller than the mean values. Thus the boundary layer approximation must be directly derived within the Reynolds equations and the transport equations. The procedure is similar to that for the laminar flow and the details may be taken from textbooks like [Burmeister, 1983] or [Anderson, et al., 1984]. For a two-dimensional flow the boundary layer equations read to:

\[\frac{\partial \overline{u}}{\partial x} + \frac{\partial \overline{v}}{\partial y} = 0 \quad \rho \left( \overline{u} \frac{\partial \overline{u}}{\partial x} + \overline{v} \frac{\partial \overline{u}}{\partial y} \right) = -\frac{dp}{dx} + \frac{\partial}{\partial y} \left( \mu \frac{\partial \overline{u}}{\partial y} - \rho \overline{u} \overline{v} \right)\]  

(10.68)

in which \(p_0\) is the pressure at the border of boundary layer to the bulk flow. A similar procedure can be performed for the transport equations and one obtains according to [Jischa, 1982] the transport equation for the shear stress and the turbulent kinetic energy equation in the form (10.69) for a 2-D flow.
The most terms in both transport equations can be measured experimentally, except for the local pressure oscillations. Fortunately the pressure oscillations do not appear in the equation for the turbulent kinetic energy.

Most flows are confined by walls and by approaching the wall the velocity oscillations hence the Reynolds shear stress approaches zero.

If we assume a fully developed 2-D turbulent flow near a wall all statistic properties depend only on the co-ordinate $y$. Since the derivative of the velocity in axial direction vanishes, the continuity equation immediately yields that the mean velocity in $y$-direction is also zero. In this specific case convective terms and the pressure are zero in the Reynolds equation and it remains:

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} + \frac{p}{\rho} \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) + \frac{\partial}{\partial y} \left( \frac{\nu}{\rho} \frac{\partial u}{\partial y} - \frac{\partial v}{\partial y} \right) = 0$$

$$u \frac{\partial k}{\partial x} + v \frac{\partial k}{\partial y} + w \frac{\partial k}{\partial z} = \frac{\partial}{\partial y} \left( \frac{k + \nu}{\rho} \frac{\partial u}{\partial y} - \frac{\partial v}{\partial y} \right)$$

$$\lim_{y \to 0} \mu \frac{\partial u}{\partial y} = \tau_w$$

Obviously only the parameters $v, \tau_u, \rho$ appear and one defines shear stress velocity $u_t$ as:

$$u_t = \frac{\sqrt{\tau_u}}{\rho} = u_0 \sqrt{\frac{f}{2}}$$

where $f$ is the friction coefficient $f = 2 \tau_u / (\rho u_0^2)$. Defining the dimensionless co-ordinates $u^*$ and $y^*$ in the way:

$$u^* = \frac{u}{u_t}, \quad y^* = \frac{yu_t}{\nu}$$

the velocity distribution close to the wall can be given in an universal manner $u^* = f(y^*)$. The solution of $f$ in the immediate vicinity of the wall is immediately obtained because the velocity fluctuations close to the wall are zero and at the wall the non-slip condition holds, so that $u^* = y^*$. This is the so-called viscous sub-layer, in which the molecular shear stress is significantly larger than the Reynolds stress. With increasing distance from the wall the Reynolds stress grows considerably and simultaneously the molecular part becomes negligible. This yields to a logarithmic expression for the dimensionless velocity in the form:
which was initially determined by Prandtl 1932. Between the viscous sublayer and the fully turbulent boundary layer a transition layer appears, for which different but mostly logarithmic functions can be used. An overview on the different definitions between viscous sublayers and fully developed boundary layer may be taken from [Shah and London, 1978].

For the transition of the anisotropic turbulent boundary layer towards the isotropic core flow the logarithmic laws loose their applicability. Within this region the so-called wake laws are introduced. There exist numerous articles for the velocity profile description in pipe flows, in which many differ only by the constants chosen for the wake profile. A comprehensive picture on the dimensionless velocity distribution in liquid metal flows can be found in the PhD thesis by [Fuchs, 1973]. Newer results can be taken from [Zagarola, 1996, 1997], [Barenblatt and Chorin, 1998] [Guo and Julien, 2003].

10.6.5 Summary

The numerical prediction of turbulent boundary layer flows is mainly possible on the basis of semi-empirical closure assumptions. They are applied directly in the Reynolds equations or in the transport equations. The applicability of closure methods of the first order is rather limited and thus mainly closure assumptions of higher order are applied, which numerically can be applied with rather small effort.

Fortunately for the formulation of semi-empirical assumptions a lot of experimental data exist and so the turbulent momentum transfer can be satisfactorily described for the forced convective liquid metal flow in simple geometries with a high degree of accuracy. Regarding the turbulent momentum transport in fully developed forced convective flows the only influencing parameter is the Reynolds number and thus pressure drop correlations, friction factors as well as production and dissipation rates can be taken from standard engineering handbooks for the individual geometry considered in the application. This is completely different to the turbulent energy exchange, since there next to the velocity data temperatures have to be determined. One should be careful to define a heavy liquid metal experiment with a small heat transfer rate to be a solely forced convective flow if only Reynolds number is quite large. This holds especially for horizontal arrangements of the experiments. Mercury experiments performed by [Gardner, 1969] or [Lefhalm, et al., 2004] have shown that even at Reynolds numbers $Re > 10^5$ buoyancy forces can become important and modifies the local flow quantities.

10.7 Turbulent energy exchange

Regarding the turbulent energy the similar procedures as for the turbulent momentum exchange can be applied. Unfortunately less experimental data are available for the turbulent energy exchange in liquid metals than for the turbulent momentum exchange where also data from other fluids can be applied. Thus, a lot of correlations appear which were derived only from one experiment sometimes with speculations on their boundary conditions. So often no uncertainty estimates can be given.

The energy equation of a steady flow of an incompressible fluid in the temperature notation writes to:

$$\rho c_p \left( v_x \frac{\partial T}{\partial x_k} \right) = \lambda \left( \frac{\partial^2 T}{\partial x_k \partial x_l} \right) \quad \text{or} \quad \rho c_p \left( \frac{\partial T}{\partial x_k} \frac{\partial T}{\partial x_l} + \frac{\partial T}{\partial y} + \frac{\partial T}{\partial z} \right) = \lambda \left( \frac{\partial^2 T}{\partial x_k^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right)$$

$$u^* = \frac{1}{C_1} \ln y^* + C_2$$

(10.75)
10.7.1 Reynolds equations for the turbulent energy exchange

When the turbulent stream involves heat transfer its instantaneous temperature $T_i$ can be decomposed according to Reynolds in a fluctuating component and a time averaged value. The time averaged component must not be confused with the bulk mean temperature $T_m$. The former is a local quantity at a discrete point, whereas the latter is a flow average quantity across the whole ducts cross-section. The Reynolds approach leads to the following equation:

$$\rho c_p \left( vy \frac{\partial T}{\partial x_i} \right) = \lambda \frac{\partial^2 T}{\partial x_i^2} - \rho c_p \frac{\partial}{\partial x_i} \left( vy T \right)$$

in which $RH$ is the apparent or virtual heat flux often referred to as the Reynolds heat flux. The Reynolds heat flux exists only due the temporal averaging of the equations. It describes a macroscopic exchange originating from the oscillating components. In contrast to the Reynolds shear stress tensor the Reynolds heat fluxes are vectorial quantities, because the transported property contains a scalar in comparison to the vectorial momentum. Also for the heat flux transport equations can be derived. In contrary to the momentum transport the turbulent energy exchange is referred to as a passive transport process.

Similar to the momentum exchange also boundary layer approximations can be applied to the energy equation. For a 2-D in the mean steady flow of an incompressible fluid they read to:

$$\rho c_p \left( u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) = \frac{\partial}{\partial y} \left( -\lambda \frac{\partial T}{\partial y} + \rho c_p v T \right)$$

10.7.2 Analogies between fluid flow and heat transfer parameters

In analogy with Newton’s law of friction for the laminar shear stress $\tau$ a law of the friction for the apparent turbulent stress $\tau_{tur}$ was introduced by [Boussinesq, 1877]:

$$\tau = -\mu \frac{\partial u}{\partial y} \quad \text{and} \quad \tau_{tur} = -\mu_{tur} \frac{\partial u}{\partial y}$$

where $\mu_{tur}$ is an apparent viscosity also referred to as a virtual or eddy viscosity. Note that the eddy viscosity is not a property of the fluid like the dynamic viscosity $\mu$, but depends on the time average flow velocity. In analogy with the molecular momentum diffusivity $\nu$, eddy diffusivity for momentum $\varepsilon_M$ is often required to characterise turbulent flow. $\nu$ and $\varepsilon_M$ are defined as:

$$\nu = \frac{\mu}{\rho} \quad \text{and} \quad \varepsilon_M = \frac{\mu_{tur}}{\rho}$$

In analogy with Fourier’s law of heat conduction for laminar flow, a law of heat conduction for turbulent flow is introduced. These laws are:

$$q = -\lambda \frac{\partial T}{\partial y} \quad \text{and} \quad q_{tur} = \lambda_{tur} \frac{\partial T}{\partial y}$$
where $\lambda_{\text{tur}}$ is an apparent (virtual or eddy) conductivity, which is also not a fluid property, but depends on the time average flow velocity as well as on the time-average bulk mean temperature. In analogy with the thermal diffusivity $\kappa$, an eddy diffusivity for heat transfer, $\varepsilon_H$ is defined.

$$
\kappa = \frac{\lambda}{\rho c_p} \quad \text{and} \quad \varepsilon_H = \frac{\lambda_{\text{tur}}}{\rho c_p}
$$

Furthermore, in analogy with the molecular Prandtl number $Pr$, a turbulent Prandtl $Pr_t$ number is introduced:

$$
Pr = \frac{\nu}{\kappa} \quad \text{and} \quad Pr_t = \frac{\varepsilon_M}{\varepsilon_H}
$$

Experiments on the turbulent Prandtl number in circular tubes exhibit that the turbulent Prandtl number depends on the Reynolds number $Re$, the molecular Prandtl number $Pr$ and the distance from the wall expressed by $(y/R)$. Such a relation in the form:

$$
Pr_t = f(Re, Pr, \frac{y}{R}) = \frac{\partial T}{\partial y} = \frac{u}{v} \frac{\partial T}{\partial u}
$$

is expected. [Eckert and Drake, 1972] collected measurements of the turbulent Prandtl number for various fluids including heavy liquid metals. They wrote, “The experimental difficulties are obviously so large, that no satisfying coherence between the individual data sets can be established for the liquid metals.” [Fuchs, 1973] describes the problems in more detail. The main error sources are:

- determination of the temperature and velocity gradients from a measured temperature and velocity distribution;
- determination of the correlation $\overline{vT}$, as well as which is in liquid metals hardly possible due to the lack of adequate measurement techniques.

Consider a fully developed turbulent flow in a circular duct. Within such a problem the resulting wall shear stress $\tau$ and the resulting heat flux $q$ can be described using the turbulent exchange quantities in the following way:

$$
\tau = (\mu + \rho \varepsilon_M) \frac{d\bar{u}}{dy} \quad \text{or} \quad \frac{\tau}{\rho} = (v + \varepsilon_H) \frac{d\bar{u}}{dy}
$$

or

$$
q = -(\lambda + \rho c_p \varepsilon_H) \frac{d\bar{T}}{dy} \quad \text{or} \quad \frac{q}{\rho c_p} = -(\kappa + \varepsilon_H) \frac{d\bar{T}}{dy}
$$

The Reynolds analogy

In fully turbulent flows $v << \varepsilon_M$ and $\kappa << \varepsilon_H$ except for the immediate vicinity of the wall. If one assumes that the turbulent energy transport has a constant ratio as the turbulent momentum transport, in the extreme case $\varepsilon_H = \varepsilon_M$ this yields immediately $Pr_t = 1$. This major assumption is called the Reynolds analogy and yields immediately for $Pr_t = 1$:  

432
\[ c_p d\overline{T} = -\frac{q}{\tau} d\overline{u} \quad (10.86) \]

This can be easily integrated, assuming at the wall non-slip for the mean velocity and the wall temperature \( T_w \) for \( \overline{T}(y = 0) \) and for the outer flow the position is used at which the mean velocity and the mean temperature is attained, i.e. \( \overline{u} = u_0 \) and \( \overline{T} = T_m \). Both quantities are defined:

\[ c_p \frac{\tau_w}{\tau} \frac{d\overline{T}}{d\overline{u}} = -\frac{q}{\tau} \frac{d\overline{u}}{d\overline{u}} \quad \text{or} \quad c_p (T_w - T_m) = \frac{q}{\tau_w} u_0 \quad (10.87) \]

Assuming the Reynolds analogy in the tube this immediately yields for the friction factor \( c_\lambda \) and for the Stanton number \( St \) the following result:

\[ c_\lambda = 8 \frac{\tau_w}{\rho u_0^2} \quad \text{and} \quad St = \frac{Nu}{Re \, Pr} = \frac{c_\lambda}{8} \quad (10.88) \]

The Reynolds analogy yields good results for molecular Prandtl numbers larger than \( Pr > 0.71 \). It is also embedded in a lot of commercial code systems using the \( k-\varepsilon \) model. It definitely fails describing the heat transport in liquid metals because the initial boundary condition of \( \varepsilon_{kl} \approx \varepsilon_{M} \) and constant is not fulfilled for this type of fluids. Thus, any approach of a constant Prandtl number assumption that means using the Reynolds analogy will lead to miscellaneous results. This problem is known since [Martinelli, 1947] and has during the last two decades been reviewed critically by several authors like [Grötzbach and Wörner, 1992], [Kays, 1994], [Carteciano and Grötzbach, 2003] or [Arien, 2004].

**The Prandtl analogy**

Within this approach the flow field is separated into two domains a viscous sublayer and a fully turbulent bulk flow. In the viscous sublayer the molecular viscosity is larger than the eddy viscosity and the molecular conductivity dominates over the eddy diffusivity, i.e. \( \nu >> \varepsilon_{M} \) and \( \kappa >> \varepsilon_{H} \). This yields:

\[ \frac{\tau}{\rho} = \nu \frac{d\overline{u}}{dy}, \quad \frac{q}{\rho c_p} = -\kappa \frac{d\overline{T}}{dy} \quad \text{and} \quad c_p d\overline{T} = -Pr \frac{q}{\tau} d\overline{u} \quad (10.89) \]

The relations can be integrated from the wall to the border of the laminar sublayer, for which \( \overline{u} = u_1 \) and \( \overline{T} = T_1 \) is assumed. For the fully turbulent bulk the model takes use of the Reynolds analogy with the assumptions \( \nu << \varepsilon_{M} \) and \( \kappa << \varepsilon_{H} \) and using them the Eqs. (10.85) can be integrated from the border of the sublayer towards the bulk, which yields the result:

\[ c_p (T_w - T_m) = \frac{q}{\tau} u_0 \left[ 1 + \frac{u_1}{u_0} (Pr - 1) \right] \quad (10.90) \]

The velocity at the border of the viscous sublayer in direction of the bulk is known since there \( u^* = y^* \) holds. Setting \( y^* = 5 \) the relation (10.91) known as Prandtl analogy is obtained, which reads for the Stanton number to:

\[ St = \frac{Nu}{Re \, Pr} = \frac{c_\lambda}{8} \frac{1}{1 + 5\sqrt{c_\lambda} / 8(Pr - 1)} \quad (10.91a) \]
For $Pr = 1$ the Prandtl analogy is similar to the Reynolds analogy. The impact of the molecular Prandtl number is reflected by taking it into account in the viscous sublayer. The factor 5 is arbitrary. But, due to the increase of the turbulent Prandtl number with decreasing molecular Prandtl number, as observed in numerous experiments, the Prandtl analogy is only very restricted applicable to liquid metal flows. The largest hint is the assumption that except for the viscous sublayer the turbulent Prandtl number is set to unity, although the thermal boundary layer is considerably larger than the viscous one.

V. Karman analogy

Following the ideas of Prandtl, v. Karman divided the flow field instead of two into three layers, the viscous sublayer ($y^+ < 5$) a transition layer ($5 < y^+ < 30$) and the turbulent wake ($y^+ > 30$). In the intermediate transition layer he assumed an identity of the molecular and the turbulent quantities, i.e. $v = \varepsilon_{M}$ and $\kappa = \varepsilon_{H}$, and obtained for the Stanton number the following relation. The exact derivation may be taken from the book of [Gebhardt, 1971]:

$$St = \frac{Nu}{Re Pr} = \frac{c_\varepsilon / 8}{1 + 5\sqrt{c_\varepsilon / 8(Pr - 1 + \ln(5Pr + 1)/6)}}$$

Further analogies

[Martinelli, 1947] extended the three layer model of v. Karman in the way that he considered both the molecular heat conductivity and the eddy diffusivity in the full turbulent range. Using this approach his analogy is applicable also to liquid metals. The considerations of Martinelli [Martinelli, 1947] and especially its restrictions are extensively discussed in the books of [Rohsenow and Choi, 1961] as well as in [Knudsen and Katz, 1958]. The results obtained consist of a number of tables. [Rohsenow and Choi, 1961] even extended Martinelli’s ideas by implementing a relation of $Pr_t = f(Pr)$. However, a comparison of the results with the experiment show only satisfactory results for Peclet number larger than $Pe > 700$. Moreover, the turbulent Prandtl number remains space independent, which does not hold for liquid metals as the following paragraph denotes.

10.7.3 Experimental observations of the turbulent heat transport

The equation (10.84) in particular makes clear that to evaluate the turbulent Prandtl number at any point it is necessary to measure four quantities: the turbulent shear stress, the turbulent heat flux, the velocity gradient and the temperature gradient. This is the reason why direct measurements of turbulent Prandtl numbers in duct flows are relatively scare and hardly available in boundary layers.

Despite the large experimental difficulties it is clear that the turbulent Prandtl number is larger than unity in case of the liquid metals, because liquid metals possess a large molecular conductivity compared to their molecular viscosity. A turbulence parcel will transfer in liquid metals easier energy than momentum to the adjacent fluid. Thus, the turbulent Prandtl number should increase with decreasing molecular Prandtl number. There is an influence of the wall distance ($y/R$) on the turbulent Prandtl number in fully developed flows. In the majority of the experimental investigations $Pr_t$ seems to decrease with increasing distance from the wall, see [Azer and Chao, 1960] or [Davies, 1969]. For the fully developed turbulent flow in circular tubes the local turbulent Prandtl number $Pr_t$ was evaluated in detail by [Fuchs, 1973] in sodium with a molecular Prandt number $Pr = 0.007$ as a function of $y/R$. The experimental results are depicted in Figure 10.7.1(a). This general tendency is supported by the measurements of [Sleicher, et al., 1973] or [Brown, et al., 1957].
Besides the dependence of the turbulent Prandtl number on the radial co-ordinate the dependence of the measured mean turbulent Prandtl number $Pr_{tm}$ on the molecular Prandtl number seems to be even larger, as depicted in Figure 10.7.1(b). The experimental data on the mean turbulent Prandtl number define show a quite large scatter for the liquid metals, which can be partially be explained by the reasons mentioned in [Fuchs, 1973]. Another aspect may be also the fact of the determination of the mean turbulent Prandtl number $Pr_{tm}$. For an exact formulation it should be gained from the Lyon-Integral [Lyon, 1951] in the form:

$$\int_0^r \frac{u}{r} \left( \frac{\varepsilon M}{Pr} + \frac{1}{Pr_t} \right) dr = \int_0^r \frac{l}{Pr} \left( \frac{\varepsilon M}{Pr} + \frac{1}{Pr_t} \right) dr$$

and assuming a constant molecular Prandtl number in the cross-section of interest one gets:

$$Pr \frac{\varepsilon M}{Pr} \frac{l}{Pr_t} = \frac{Nu}{Nu_{min}} - 1$$

where $Nu_{min}$ is the Nusselt number in case of pure heat conduction. Some authors tried based on different assumptions to derive formulas for the mean turbulent Prandtl number. This aspect will be discussed in the context of the different closure models in the next section.

Figure 10.7.1. (a) Measured turbulent Prandtl number $Pr_t$ as a function of the dimensionless distance ($y/R$) in a fully developed turbulent circular duct flow with a constant wall heat flux ($q_w = \text{const.}$) from [Fuchs, 1973]. b.) Measured mean turbulent Prandtl number $Pr_{tm}$ for different molecular Prandtl numbers $Pr$ for a fully developed turbulent circular duct flow with a constant wall heat flux ($q_w = \text{const.}$) for two different Reynolds numbers $Re = 2 \times 10^4$ (open symbols) and $Re = 10^5$. The experimental data are from [Fuchs, 1973] for $\square$Na, [Buhr, et al., 1968] for O NaK and $\Delta$Hg, [Subbotin, et al. 1962] $\bigcirc$Na, $\bigcirc$PbBi, [Sleicher, 1958] $\ast$air, [Allen and Eckert, 1964] $+$water.
From the experimental observations the following statements on the mean turbulent Prandtl number $Pr_{tm}$ can be made:

- For $Pr \geq 1$ (air, water, oil, etc.) the turbulent Prandtl number seems to be constant and independent of the Reynolds number and molecular Prandtl number.
- The influence of the Prandtl number and the Reynolds number increases both with decreasing Prandtl number and decreasing Reynolds number.
- The turbulent Prandtl number increases with decreasing Prandtl number and decreasing Reynolds number.

### 10.7.4 Closure methods for the turbulent heat flux

The knowledge of the turbulent Prandtl number is a central problem of all theoretical considerations concerning the turbulent heat transfer in two-dimensional boundary layers or in duct flows. A large number of models have been published in the past which address the prediction of the turbulent Prandtl number $Pr_t$ for such situations. There is a very strong influence of the molecular Prandtl number on the value of $Pr$, for fluids with very low Prandtl numbers (liquid metals). Additionally, here is an influence of the wall distance on the value of the turbulent Prandtl number which tends to increase $Pr$, close to the wall. This increase in $Pr$, near the wall is especially important for high Prandtl number fluids because of the very thin thermal boundary layer. Outside this thin layer near the wall the turbulent Prandtl number seems to be constant for $Pr > 1$. Because of the strong dependence of $Pr_t$ on molecular Prandtl number for low Prandtl number fluids (liquid metals) effort has been taken in the past to develop prediction models for $Pr_{tm}$, which are able to take the dependence of $Pr_{tm}$ on the molecular Prandtl number as well as the dependence of $Pr_{tm}$ on the wall distance into account.

In principle all the proposals can be divided into mainly four classes (of course containing numerous amount of subclasses):

- a) semi-empirical or empirical closure methods of zero and first order;
- b) turbulent Prandtl number from analytic solutions;
- c) modelling of the turbulent heat flux by means of transport equations at different levels;
- d) direct numerical simulation of the whole set of the time-dependent Navier-Stokes equations.

The length of this chapter extends a little compared to the previous ones. But the currently excessive use of numerical simulation tools to design critical components of liquid metal cooled devices in many technical fields requires a principle understanding of what is modelled in the individual closure assumptions for the turbulent heat fluxes. The type of this modelling plays a decisive role in the analysis of the results. It is clear, that not all the details of the modelling can be described within this context. However, the main ideas, the assumptions and the approaches yielding to the specific results for the different types of closure methods are flash-lighted. Moreover, the limiting parameter range for their validity is given as far as known to the author. Hopefully, a list of the most relevant literature is cited in this context. At the end of each section a “sometimes” rather personal assessment is given on the individual class of closure type.

**a) Semi-empirical closure methods of zero and first order**

Reviews of the existing work of these types of closure methods can be found in the overview article by [Reynolds, 1975] or in [Kays, 1994]. Within these types of models a whole branch of assumptions is hided.
The simplest ones are purely empirical correlations, in which the turbulent Prandtl number is mainly fitted to experimental data from various experiments, as e.g. by [Notter, 1969]. Some workers, though aware of attempts to predict the dependence of the eddy diffusivity ratio an molecular diffusivities and position within the flow, have rejected these analytical results, in view of the contradictions among the several models, between models and experiments, and even between different experiments. In this view [Kunz and Yerazunis, 1969] adopted for the for the turbulent Prandtl number of turbulent liquid metal flows in a circular duct:

\[ Pr_t = \left( \frac{2}{3} \right) \exp \left[ 0.9 \left( \frac{e_{M}}{v} \right)^{0.64} \right] \]  \hspace{1cm} (10.94)

With this they accept deviations of ±0.5 from the experiments they consider and further, it does not contain a dependence of the radial co-ordinate. Again, in the view of the scatter of their measurements, [Quarmby and Quirk, 1972, 1974] felt that it was impossible to isolate the dependence of the turbulent Prandtl number on the molecular Prandtl number and the duct Reynolds number. Nevertheless, they found an important variation across the pipe and formulated for their individual experiment the relation:

\[ Pr_t = \left( 1 + 400^{-y/R} \right)^{-1} \]  \hspace{1cm} (10.95)

This yields a turbulent Prandtl number near the wall of \( Pr_t = 0.5 \), which is considerably to low for liquid metal flows [see Figure 10.7.1(a)], while close to the ducts centre a value of \( Pr_t \approx 1 \) is obtained, which is acceptable for \( Re > 5 \times 10^4 \). These purely empirical results offer neither practical nor fundamental advantages. And as matter of fact the effort spent on these methods ended around the late seventies.

A more theoretical approach offered the individual mixing length models already mentioned in the context of the analogies between heat and mass transfer. These analyses seek to account for the exchange of momentum and heat transfer between the instantaneous surroundings and a lump of fluid which moves across gradients of velocities and temperature. At the end of its journey the lump (mostly considered to be a sphere) is assumed to mix instantaneously with the surrounding fluid; the transfer rate is calculated using the terminal properties of the moving element. Clearly, these types of models are inconsistent in that no account is taken of that fraction of the transferred (heat or momentum) flux which is conveyed only part way along the mixing length. This implies more or less a proportional relation between turbulent heat and turbulent momentum flux known from the Reynolds analogy. Several types of mixing length models were proposed ranging from the beginning fifties up to the end of the sixties. The most famous are the Jenkins type mixing models after [Jenkins, 1951] with several modifications, which are listed in Table 10.7.1 and basically yield the turbulent Prandtl number as a function of the molecular Prandtl number and \( \varepsilon_{M}/v \). They do only marginally contain a local dependence of \( Pr_t \) on \( y/R \).

<table>
<thead>
<tr>
<th>Author</th>
<th>Functional form</th>
<th>Empirical constants</th>
<th>Validity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jenkins, 1951</td>
<td>( f(Pr, \varepsilon_{M}/v) )</td>
<td>0</td>
<td>All ( Pr )</td>
</tr>
<tr>
<td>Sleicher and Tribus, 1957</td>
<td>( f(Pr, \varepsilon_{M}/v) )</td>
<td>( f(\varepsilon_{M}/v) )</td>
<td>All ( Pr )</td>
</tr>
<tr>
<td>Roshenow and Cohen, 1960</td>
<td>( f(Pr) )</td>
<td>1</td>
<td>( Pr &lt;&lt; 1 )</td>
</tr>
<tr>
<td>Tien, 1961</td>
<td>( f(Pr, \varepsilon_{M}/v) )</td>
<td>1</td>
<td>All ( Pr )</td>
</tr>
<tr>
<td>Senechal, 1968</td>
<td>( f(y^{2}v'/(l \kappa)) )</td>
<td>1</td>
<td>( Pr &lt; 1 )</td>
</tr>
</tbody>
</table>

Table 10.7.1. Different Jenkins type mixing length models and their range of validity for the turbulent Prandtl number \( Pr_t \).
The other class of mixing length models is formed by the Deissler type models after [Deissler, 1952], which is focussed on mainly small Prandtl number fluids as the liquid metals. They take into account only the heat transfer from the moving element and relate the length scale of an imaginary fluid sphere in the temperature gradient field to the mixing length. On this scale only molecular diffusion is assumed. These types of models are listed in Table 10.7.2 with their range of validity. A problem here is similar as in the Jenkins models that the velocity field is coupled directly to the temperature field, although knowing from the experiments that the statistical features of both are different.

### Table 10.7.2. Different Deissler type mixing length models and their range of validity for the determination of the turbulent Prandtl number $Pr_t$

<table>
<thead>
<tr>
<th>Author</th>
<th>Functional form</th>
<th>Empirical constants</th>
<th>Validity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deissler, 1952</td>
<td>$f(Pr)$</td>
<td>1</td>
<td>$Pr &lt;&lt; 1$</td>
</tr>
<tr>
<td>Lykoudis and Touloukian, 1958</td>
<td>$f(Pr)$</td>
<td>1</td>
<td>$Pr &lt;&lt; 1$</td>
</tr>
<tr>
<td>Aoki, 1963</td>
<td>$f(Pr Re^{2.25})$</td>
<td>1</td>
<td>$Pr &lt;&lt; 1$</td>
</tr>
<tr>
<td>Mizushina and Sasano, 1963</td>
<td>$f(Pr, \varepsilon_d/v)$</td>
<td>3</td>
<td>$Pr &lt; 1$</td>
</tr>
<tr>
<td>Mizushina, et al., 1969</td>
<td>$f(Pr, \varepsilon_d/v, aT)$</td>
<td>3</td>
<td>$Pr &lt; 1$</td>
</tr>
<tr>
<td>Wassel and Catton, 1973</td>
<td>$f(Pr, \varepsilon_d/v)$</td>
<td>3</td>
<td>All $Pr$</td>
</tr>
</tbody>
</table>

The more advanced mixing length models adopt a more sophisticated picture of the turbulent activity. Thus the defining feature of this category is not the use of an immutable mixing length but the introduction of a discrete element which gains or looses heat and momentum as it moves through the bulk of the fluid. Nevertheless, also this analysis is constrained by the assumption of a basic analogy between momentum and heat transfer, at least in its statistical behaviour. In the article by [Reynolds, 1975] the individual aspects of these type of models are discussed as well as their advantages and disadvantages in use. They seem to fit quite well for the turbulent Prandtl number in duct and plate flow but do not generally account for the temporal behaviour of the temperature and flow field. These more advanced models are listed in Table 10.7.3.

### Table 10.7.3. Different varied mixing length models and their range of validity for the determination of the turbulent Prandtl number $Pr_t$

<table>
<thead>
<tr>
<th>Author</th>
<th>Functional form</th>
<th>Empirical constants</th>
<th>Validity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azer and Chao, 1960</td>
<td>$f(Pr, Pr, y/R)$</td>
<td>1+</td>
<td>$Pr &lt;&lt; 1$</td>
</tr>
<tr>
<td>Buleev, 1962</td>
<td>$f(Pr, Re, geometry)$</td>
<td>5</td>
<td>All $Pr$</td>
</tr>
<tr>
<td>Dwyer, 1963</td>
<td>$f(Pr, \varepsilon_d/v)$</td>
<td>2</td>
<td>$Pr &lt;&lt; 1$</td>
</tr>
<tr>
<td>Tyldesley and Silver, 1968</td>
<td>$f(Pr)$</td>
<td>1</td>
<td>All $Pr$</td>
</tr>
<tr>
<td>Tyldesley, 1969</td>
<td>$f(Pr, ?)$</td>
<td>2</td>
<td>All $Pr$</td>
</tr>
<tr>
<td>Ramm and Johannsen, 1973</td>
<td>$f(Pr, Re, geometry)$</td>
<td>5+</td>
<td>All $Pr$</td>
</tr>
</tbody>
</table>

These semi-empirical types of closure methods contains also another group of models which is based on the analysis of the Reynolds equations without the direct formulation of transport equations. Additionally, [Kays and Crawford, 1993] developed a prediction model for $Pr$, which can be used for all molecular Prandtl numbers. The model contains two empirical constants which must be determined from available experimental data. [Cebeci, 1973] adopted van Driest’s idea of near-wall damping of the mixing length to propose a turbulent Prandtl number concept. This model was extended by [Chen and Chio, 1981] for liquid metal flow in pipes by incorporating the enthalpy thickness $\delta_T$ in $Pr_t$. Although the predictions of Chen and Chio agree well with measured Nusselt numbers for liquid metal flows, their model has the disadvantage that an additional nonlinearity is introduced into the
energy equation by using the enthalpy thickness $\delta_T$, in $Pr_t$. This restricts the possibility of analytical solutions of the energy equation for hydrodynamically fully-developed flows. Furthermore, the von Kármán constant is changed in the mixing length expression for their calculation. This might lead to misleading results for larger molecular Prandtl numbers.

**Summary on semi-empirical or empirical closure methods of zero and first order**

All semi-empirical closures for the turbulent heat flux independent of their order do not give detailed insight in the turbulent exchange mechanisms between the velocity fluctuations and the temperature oscillations. For engineering purposes some of them can be applied to assess the heat exchange, but one should be careful on the model, its validity and the empirical constants chosen, because they often apply only for one fluid in a rather limited parameter field. By nature the Reynolds analogy can give only reliable results for large Reynolds numbers, in which the thermal boundary layer remains small and the turbulent Prandtl number tends to unity. As soon as one arrives to lower Reynolds numbers, this analogy leads to inaccurate results. This should be taken into account also for numerical simulations using the $k$-$\varepsilon$ model without an additional turbulent heat flux modelling. As benchmark studies have shown, see [Arien, 2004] this can lead to severe discrepancies.

**b) Turbulent Prandtl number from analytic solutions**

[Yakhot, et al., 1987] present an analytic solution based on what they call the “renormalisation group analysis method” and this result is apparently devoid of any empirical input. The relative simple equation reads to:

$$Pr_{eff} = \left( \frac{1+\varepsilon_M/\nu}{Pr_t + \frac{1}{Pr}} \right)$$

(10.96)

It is not clear whether this result is expected to be valid over the entire boundary layer or only in the region where the logarithmic law holds. It is remarkable that the results obtained with that relationship matches the nearly all experimental observations quite well. And it seems even to work for higher molecular Prandtl number. [Kays, 1994] fitted the relation (10.96) by an asymptotic curve in the form:

$$Pr_t = 0.7 \frac{Pe_t}{Pe_t + 0.85} \quad \text{with} \quad Pe_t = (\varepsilon_M/\nu) Pr$$

(10.97)

where $Pe_t$ is the turbulent Peclet number. It looks similar like a suggestion performed by [Reynolds, 1975] but in that case $Pr_t$ is an average throughout the whole boundary layer.

[Lin, et al., 2000] modified the renormalisation group analysis performed by [Yakhot, et al., 1987]. Within the model a quasi-normal approximation (see [Chou and Chin, 1940]) is assumed for the statistical correlation between the velocity and temperature fields. Due to the statistical approach the different time scales of the temperature fluctuations and the velocity fluctuations remain in the model and are coupled together by the wave number $k$. A differential argument leads to derivation of the turbulent Prandtl number $Pr_t$ as a function of the turbulent Peclet $Pe_t$ number, which in turn depends on the turbulent eddy viscosity $\varepsilon_M$. The functional relationship between $Pr_t$ and $Pe_t$ is comparable to that of [Yakhot, et al., 1987] but it contains in contrast to the Yakhot, et al. solution the spectral properties of both oscillating fields. But, the resulting formula for the effective turbulent Prandtl number $Pr_{eff}$ is very close to Eq. (10.96). It reads to:
\[
\left[ \frac{\left( Pr_t^{\prime} \right)^2 - 1}{\left( Pr_t^{\prime} \right)^2 - 1} \right]^{\frac{2/3}{\varepsilon_m / \nu}} = \frac{1}{\left( 1 + \varepsilon_m / \nu \right)} \] 
\] with \[ Pr_{\text{eff}} = \frac{\left( 1 + \varepsilon_m / \nu \right)}{\left( Pr_t^{\prime} \right)^2 + 1} \] (10.98)

The apparent resemblance between the formulas (10.96) and (10.98) is quite remarkable not only because of the similarity in mathematical structure, but because the results are basically derived entirely from different approaches to renormalization group analysis of turbulence. \( Pr_t \) can be represented in terms of \( Pe_t \) for any given molecular Prandtl number \( Pr \). A comparison with the direct numerical simulation results (in which the whole set of time dependent Navier-Stokes equation is solved) of [Kasagi, et al., 1992] and [Kim and Moin, 1987] shows excellent agreement for a Prandtl number of \( Pr = 0.1 \). Also a comparison of the results with the experimental data taken from [Bremhost and Krebs, Sheriff and O’Kane, and Fuchs, 1973] all measured in liquid sodium at the centreline of thermal turbulent pipe flow shows excellent agreement, see Figure 10.7.2(a). Next, they noticed that the Peclet number \( Pe_t \) is a thermal analogy of the Reynolds number. The reason why \( Pr_t \) always tends to 1 as \( Pe_t \) becomes sufficiently large would be that at this time the thermal flow turbulence is completely convection dominated and the temperature field \( T \) responds immediately to any change of the velocity field \( v \).

Figure 10.7.2. a.) The turbulent Prandtl number \( Pr_t \) versus the turbulent Peclet number \( Pe_t \) plotted based on Eq. (10.98) for liquid sodium (\( Pr = 0.007 \)) in comparison with experimental data measured by [Bremhost and Krebs, 1992, □], [Sheriff and O’Kane, 1980, △] and [Fuchs, 1973, O]. b.) The scaling law of the thermal energy spectrum \( E_{\text{Hum}}(k) \) versus the normalised wave number \( k/k_0 \) for \( Pr << 1 \) after [Lin, et al., 2000] in comparison with experiments by [Boston and Burling, 1972].

[Batchelor, 1958a, b] was the first to propose scaling laws for the thermal energy spectrum for \( Pr << 1 \) and \( Pr >> 1 \), respectively, leaving a proportional constant \( C_B \) undetermined. Subsequently, many authors have tried to estimate or measure the value of \( C_B \) under various flow conditions. In theory, [Kraichnan, 1971] had the estimate \( C_B = 0.208 \), and [Gibson and Schwarz, 1963a] had the estimate \( C_B = 0.9 \), while [Yakhot, et al., 1987] obtained \( C_B = 1.16 \) according to their \( \varepsilon \)-based renormalisation group analysis. [Kerr, 1990] obtained numerically the value \( C_B = 0.6 \). In experiment, [Gibson and Schwarz, 1963b] had \( C_B = 0.35 \), [Grant, et al., 1968] obtained \( C_B = 0.31 \), and [Boston and Burling, 1972] got \( C_B = 0.81 \).
Due to the retaining of the spectral information in the model by [Lin, et al., 2000] the scaling laws for the thermal energy spectrum \( E_{\text{tur}} \) versus the wave-number \( k \) can be obtained. Such a thermal energy spectrum as a function of the normalised wave-number is depicted in Figure 10.7.2(b). It is visible that in the inertial-convective range the thermal energy spectrum follows a power law of \(-5/3\) and in the inertial-conductive range of a slope of \(-17/3\) is obtained. Especially, the latter is different to large Prandtl number fluids, where in the inertial conductive domain a slope of \(-1\) is observed, see experiments by [Grant, et al., 1968]. Thus, an essential result of the renormalisation group analysis is that the Batchelor constant is not a universal constant, but depends on the shape of the actual thermal energy spectrum.

The usual Smagorinsky model is used for the large-eddy simulation of the Navier-Stokes equation. One can construct a parallel model for turbulent transport of the passive scalar, which yields that constant \( C_p \) depends on \( Pr_t^{-1/2} \) and on the wave number \( k \).

In order to model the turbulent thermal transport process at a wall boundary the surface renewal concept initially introduced by [Danckwerts, 1951] can also be used. This was recently modified by [Tricoli, 1999]. The basic assumption considers the surface to be covered by a mosaic of laminar flowing patches of fluid, where transport occurs only by molecular diffusion. These fluid patches are supposed to be periodically replaced by new ones “surface renewal model” or to form viscous layers that periodically grow and collapse “growth-breakdown model”. These are unsteady state 1-D models. It has also been proposed that the fluid patches are arranged in a regular repetitive pattern of steady state boundary layers developing for a given length. These simple models are able to explain a number of qualitative features observed in turbulent transport. The model derived by [Tricoli, 1999] appeal to postulated mechanistic pictures of turbulence and the concepts and the quantities involved have no fundamental relationship with the correlated turbulent fluctuations, the sole quantities that actually determine turbulent transport. He constructed a theory able to predict turbulent heat transport from fundamental information, namely the thermal diffusivity and the normal turbulence intensity in the fluid bulk. This theory applies to heat transfer in turbulent incompressible flow for \( Pr << 1 \). His approach is based on the primary ingredients of turbulent transport, i.e. the turbulence fluctuation and the molecular momentum or heat diffusivity and does not contain empirical expressions for such quantities “eddy diffusivity models” or postulates a physical picture of the transport mechanism at the wall surface “surface renewal”. The predictions show an excellent agreement with available experimental data and empirical correlations for the turbulent heat transport in liquid metal flows in pipes. The most remarkable results of this approach refer to a relationship of the Nusselt numbers in a fully developed turbulent circular duct flow with different thermal boundary conditions. This relation valid for \( Pe > 10^3 \) reads to:

\[
\frac{Nu_{(r=\text{const})}}{Nu_{(q=\text{const})}} = \frac{12}{\pi^2} \quad (10.99)
\]

Summary on turbulent Prandtl number derivations from analytic solutions

The analytic class of solutions for the turbulent Prandtl number may be difficult to handle in the context of a numerical treatment of a commercial code package. But it gives important results to the near wall behaviour of the heat flux and thus contributes considerably to the treatment of the thermal wall functions. Another aspect is that, especially within the renormalisation group analysis, the temporal behaviour of the temperature field is still a part of the final result. This allows verifying the validity of direct numerical simulations (DNS), which are in principle exact but may use a too coarse grid. Only the analytic solutions are able to provide near wall data of the kinetic and thermal energy spectrum, because current measurement technologies are still in a stage where they hardly can resolve the viscous and thermal boundary layers simultaneously and the analytic solutions are able to provide assessments...
in complex geometries, which are currently not accessible with a direct numerical simulation. Unfortunately, for engineering applications to assess a mean turbulent heat transport form a wall this type of analysis is time consuming and requires a lot of effort.

c) Modelling of the turbulent heat flux by means of transport equations at different levels

The modelling of the turbulent heat fluxes by means of the transport equations contains in some sense also to the semi-empirical methods, because the development of each transport equation generates a set of constants a priori not known. These constants can be either experimentally determined or calculated by exact solutions (analytic ones or a direct numerical simulation). The modelling of the turbulent heat flux transport equations follows the same systematic scheme as shown in the section of the turbulent momentum exchange.

A first proposal to model the turbulent heat fluxes using transport equations was made by [Jischa and Rieke, 1979]. The final form of their transport equation for boundary layer type flows reads for the heat flux in wall normal direction to:

\[
\frac{1}{u} \left( \frac{\partial (uT)}{\partial x} + \frac{\partial (vT)}{\partial y} \right) + v^2 \frac{\partial T}{\partial y} - u \frac{\partial p}{\partial x} \frac{1}{\rho} \frac{\partial T}{\partial x} + \frac{\partial (Pr + 1)}{\partial y} \frac{\partial T}{\partial x} \frac{p}{\rho} \frac{\partial T}{\partial y} + \frac{\partial v}{\partial y} \left( vT + \ldots \right) = 0 \tag{10.100}
\]

Generally, all types of turbulent transport equations exhibit the same structure consisting of convective terms, turbulence production, dissipation, redistribution and finally diffusion. Every of the newly modelled transport equations contain correlation or time averaged products not known. The challenging task after formulating these flux transports, dissipation or destruction terms is to model the unknown correlations or gradients in an appropriate manner. This can be conducted in form of a gradient approach like the Boussinesq approach for the shear stress, where \( u \nu \sim \partial \bar{u}/\partial y \) was set, or even an additional transport equation if a simple gradient approach can not match all the transport processes taking place in the individual problem.

In the work by [Jischa and Rieke, 1979 and 1982] the turbulent fluctuations \( v^2 \) are assumed to be proportional to the turbulent kinetic energy \( k \) and for the dissipation of the turbulent kinetic energy the Prandtl mixing length approach has been used. The latter is problematic with respect to liquid metals since the molecular heat conduction is not negligible. Finally, the dissipation of the gradients of the velocity and temperature fluctuations were set to be proportional to the turbulent heat fluxes in the form \( (\nu / Pr) \partial v \partial T = C_D (\nu / Pr) \bar{v} \bar{T} / L^2 \), where \( C_D \) is a constant and \( L^2 \) the square of a characteristic length. All these assumptions yield finally to a simplified transport equation, in which the turbulent heat flux is a function of the temperature gradient. Although this model is rather crude, since the turbulent heat flux model is only taking into account a forced convective transport, it exhibits the dependence of the turbulent Prandtl on the distance from the wall and on the Reynolds number. As a disadvantage it should be clearly noted that the thermal eddy diffusivity \( \varepsilon_H \) is still linked to the momentum diffusivity \( \varepsilon_M \) assuming a similar statistical behaviour of the turbulence and that it is valid only for high Peclet numbers in purely forced convective flows. Thus, any kind of mixed or even buoyant flow can not be treated.

In the past decade a considerable effort has been spend on the development of a more detailed modelling of the turbulent heat fluxes, the turbulent temperature variance \( \bar{T}^2 \) and its dissipation or destruction \( \varepsilon_T \). A first order four-equation type model has been developed by [Nagano, et al., 1988, 1994 and 1995], which was able to represent the physics in more detail, but required of course data for
the unknown constants appearing in the new transport equations and information on the statistical behaviour of the fluctuations near the boundaries especially the walls. Especially, close to the wall or in mixed and even more in buoyant convective flows the turbulence field is strongly anisotropic, which does not allow to match the turbulent shear stresses $\tau^2$ with the turbulent kinetic energy $k$, see [Durbin, 1993a]. The details of the more advanced shear stress modelling close to the walls may be taken from [Durbin, 1993a and b], [Manceau, et al., 2000], [Oi, et al., 2002] or [Speziale and So, 1998].

Also the modelling of the turbulent heat flux evolution equations is still problematic and the reported results are only slightly better than obtained with lower order closures which based on the eddy diffusivity formulation, see [Nagano and Kim, 1988]. Thus in many forced convective problems the two-equation approaches accounting for the temperature variance $\overline{T^2}$ and its destruction $\varepsilon_T$, are current state of the art, see [Grötzbach, et al. 2004] and [Karcz and Badur, 2005]. A lot of attention must be paid to the destruction rate of temperature variance transport equation and this especially close to the wall. Different approaches are generally employed to predict the generation of $\varepsilon_T$. The details on the different approaches may be taken from [Sommer, et al., 1992], [Abe, et al. 1995], [Shikazono and Kasagi, 1996], [Deng, et al., 2001] or in a comprehensive study by [Nagano, 2002].

Next to wall near flows also any buoyancy influenced flow exhibits a strong anisotropy. In such types of flow even a second order description of the turbulent transport of heat should be applied [see Grötzbach, et al., 2004], which means the use of independent transport equations for the three components of the turbulent heat flux vector. These kinds of turbulence models called “Turbulent model for buoyant flow mixing” (TMBF) proposed by [Carteciano, et al., 1997], [Carteciano and Grötzbach, 2003] belong to this class of models.

**Summary on modelling of the turbulent heat flux by means of transport equations at different levels**

Any computational fluid dynamic calculation, which is conducted to assess the liquid metal heat transfer in turbulent flows must be performed by a skilled user, which is aware of the specific features appearing in liquid metal flows. In purely forced convective flows, which may even not appear for hydraulic Reynolds number beyond $Re > 10^5$ (see [Gardner, 1968] or [Lefhalm, 2004]) a $k-\varepsilon$ model may exhibit sensible results if the thermal wall function formulation chosen is correct and applies for the problem considered. In strongly anisotropic flows liquid metal flows associated with heat transfer the $k-\varepsilon$ model using a constant turbulent Prandtl number of $Pr_t = 0.9$ (Reynolds analogy) yields unphysical results. In this context higher order closure approaches are necessary in which the turbulent heat fluxes are modelled in such a sense that the transport equations contain the statistical features of the thermal field. By performing such an approach unknown triple correlations and constants are generated. The spatial distribution of the correlations may be directly evaluated in benchmark experiments, which is due to the limited capability of the currently available measurement techniques difficult. More often the correlations and constant are determined by the comparison of the modelling data with the exact solution obtained by means of direct numerical simulation.

d) **Direct numerical simulation (DNS)**

The direct numerical solution of the time dependent Navier-Stokes equations represents in principle an exact solution of the problem. Although the progress in memory storage capacity and computing speed increased considerably in the past decade the application of a DNS is still limited to rather heat transfer problems in simple geometries. Nevertheless, the progress made in the computer technology allows now to perform DNS-calculations which are not only slightly turbulent as the first ones by [Kim and Moin 1989], where it was difficult due to the low Reynolds number to detect the logarithmic region of the velocity profile. The DNS performed in the recent years where focused to
study the effect of the Prandtl number both in case of isotropic turbulence [Kasagi, et al., 1993], in near wall flows ([Kawamura, et al., 1998, 1999] or [Piller, et al. 2002]) and in buoyancy governed flows [Otic, et al., 2005] (here only a few publications of exemplary nature are cited). An immediate result of these computations is the spatial and temporal dependence of the statistical properties of the thermal and the momentum field on the different boundary conditions, which is especially experimentally not accessible. Thus, the DNS is currently the only available tool to qualify and verify the completeness and quality of computer codes based on a transport equation modelling. It reveals their modelling deficits and offers the possibility to model more adapted higher order closures. In this sense DNS can be conceived as a complementary tool for a more advanced turbulence modelling for technical and engineering applications, from which the DNS is still far away.

10.7.5 Heat transfer correlations for engineering applications

All the heat transfer correlations referred to in this subsection are valid for the single-phase heat transfer of a turbulent liquid metal flow in a specified geometry. They are gained by experiments performed since the late forties up to the present. For many of the described and shown heat transfer correlations the whole set of boundary conditions were not available, so that a final judgement on the quality of the obtained data can not be drawn. Especially, data on the homogeneity of the produced wall heat flux, the temperature uncertainty, the inlet-conditions for the flow field and the methodology to determine if the flow or the temperature field is fully developed or not. Another aspect in this context is the question, how the Nusselt number is determined. In many publications it is unclear if this has been performed using a global or a local method.

The survey of the heat transfer correlations does not cover the uncertainties of the turbulent velocity profiles, since for most of the liquid metal experiments conducted in the past, except for a few rather specific ones, a full set is not available.

Taking into account the numerous heat transfer correlations being on the “market” this subsection tries to outline, how large the uncertainty margin for the individual correlation is and where the deviation to the other arise from. But, before turning into the technical description of the forced convective heat transfer processes some critical remarks to the terminology forced convection should be mentioned.

Despite the considerable effort made in the computational fluid dynamics, for engineering purposes, heat transfer correlations play still a significant role. It may be to assess, how much heat can be transferred in a particular set-up or they may be used in the context of a system analysis. Many technical configurations consist of several devices and each of them acts as a heat sink (heat exchanger) or a heat source (by viscous dissipation as a valve or a mechanical pump, by direct electric heating like an electro-magnetic pump, or the fluid flow around a the reactor thermal source). Current computational simulations are by far not capable to represent the whole set three-dimensionally. Hence, the component interaction is mainly performed by one-dimensional models taking into account the heat transfer correlations and the friction factor in the flow components in order to predict the temporal system performance in dependence of normal and abnormal operation cases.

10.7.5.1 Free convection distortion in liquid metal heat transfer

Free convection becomes important at low Reynolds numbers in liquid metals and usually influences the heat transfer by distorting the according temperature and velocity profiles from the expected symmetrical behaviour. This effect is even more emphasised for heavy liquid metals. Free
Convection distortion have been already observed by [Schrock, 1964] in sodium-potassium (NaK) for Reynolds number up to $1.6 \times 10^4$, by [Lefhalm, et al., 2003 and 2004] in lead-bismuth up to $Re = 1.1 \times 10^5$, and [Gardner, 1969] in mercury for $Re = 3 \times 10^5$ in horizontal tubes, while in vertical circular tubes [Kowalski, 1974] detected free convection distortion up to Reynolds numbers of $Re = 9 \times 10^4$. All the experimental data exhibit that the velocity profile rapidly distorts as the heat flux is increased. At high heat flux a limiting profile shape with the centreline velocity well below the mean velocity $u_0$. As a matter of this fact the experimentally determined Nusselt number in even in a "fully developed pipe flow" depends on several parameters, such as whether the pipe flow is upwards or downwards, the pipe is horizontal or vertical, the direction of the heat flux (cooled or heated) and the value of the Rayleigh number. Figure 10.7.3(a) displays the measured Nusselt number variations in dependence of the angle of the perimeter for a horizontal turbulent mercury pipe flow having free convection distortion. In an order of magnitude estimation performed by [Buhr, 1967] he introduced a parameter, say $Z$, which can be conceived as a ratio of the buoyancy forces versus the inertia forces. This parameter is defined as:

$$Z = \frac{Ra \cdot d_h}{Re \cdot L}$$

with $Ra = Gr \cdot Pr$, $Gr = \frac{d_h^3 \beta g \Delta T}{v^2}$ and $\Delta T = \frac{dT}{dx} \frac{d_h}{Re \cdot Ra}$. 

Herein, $Re$ is the hydraulic Reynolds number, $d_h$ the hydraulic diameter, $Ra$ the Rayleigh number, $Gr$ the Grashof number, $\beta$ the expansion coefficient, $g$ the gravity constant, $v$ the kinematic viscosity and $\Delta T$ the axial temperature difference. He analysed a series of vertical and horizontal heat transfer experiments in pipe flow and found that if $Z > 2 \times 10^{-4}$ free convection affects the forced convective measured Nusselt number $Nu$. Also he is mentioning that the fluid properties especially for larger temperature differences should be evaluated at the bulk mean temperature $T_m = (T_{in} + T_{out})/2$.

**Figure 10.7.3.** a.) Measured local Nusselt number at several angles of the perimeter in a turbulent mercury in a horizontal pipe with convection distortion effects from [Gardner, 1969]. b.) Dependence of the Nusselt number on the $Z$-parameter, in a vertically upward directed turbulent mercury pipe flow exhibiting free convection effects.

When the flow is dominated by forced convection, the following qualitative picture of the effects of free convection on the forced convection heat transfer is observed. Buoyancy forces enhance the turbulent heat transfer to liquid metals for downwards oriented flow while it retards it for upwards directed flow. Buoyancy forces influence the convective heat transfer indirectly through their effect on shear stress distribution in the liquid metal. In vertically downward flow, the buoyancy forces operate
against the mean flow direction and increase the isothermal shear stress near the heated surface. In contrast to the upwards flow the shear stress is reduced by the buoyancy. The increase in shear stress in the downwards flowing case leads to an increase of the turbulence production and hence will enhance the heat transfer. The opposite holds for the upward flow. If the temperature gradients are large the buoyancy effects become more and more important and the enhancement of heat transfer occurs in both upward and downward flow as observed by [Jackson, 1983]. The effects of buoyancy on heat transfer to liquid metals are for the relatively “light” alkali metals less than for ordinary fluids because of the reduced importance of turbulent eddy conduction at low Peclet numbers. For heavy liquid metals, however, due to their low viscosity they are of crucial importance.

This qualitative picture is supported by Figure 10.7.3(b), which exhibits that the Nusslet number is a function of the parameter \( Z \) – initially decreasing, then growing as \( Z \) increases. \( Z \) is essentially proportional to the applied heat flux. As the buoyancy forces become comparable to the inertia forces of the flow the Nusselt number reaches a minimum, begins to increase, and finally appears to reach a limiting value. It can be seen that the effects of free convection distortion can affect the measured value of the Nusselt number and could, therefore, explain some of the well-known scatter in the Nusselt number data for the liquid metal heat transfer. Needless to say, the effects of free convection distortion must be considered when dealing with liquid metal heat transfer systems, especially for heavy liquid metal systems.

10.7.5.2 Turbulent heat transfer in circular ducts

The turbulent heat transfer in circular ducts is one of the most often investigated configuration of the liquid metal heat transfer. Similar as in the laminar energy exchange one can distinguish between the three cases:

a) fully developed flow (either hydraulically and thermally);

b) hydraulically developing;

c) thermally developing.

a) Fully developed turbulent flow

For liquids with Prandtl number around unity both the temperature and the velocity distribution can be calculated approximately in terms of a series expansion. But, for liquids with \( Pr << 1 \) (as well as for \( Pr >> 1 \)) no closed form formulas for the temperature distribution are available either for the condition of a constant wall temperature (\( T_w = \text{const.} \)) or a constant wall heat flux (\( q_w = \text{const.} \)). A ridiculously large number of correlations, both theoretical and empirical have been developed for the heat transfer in a smooth circular duct. [Shah and Johnson, 1981] put many of them together in tabular form, which is extended by the correlations known to the authors in the context of this handbook. The correlations for constant wall temperature (\( T_w = \text{const.} \)) are displayed in Table 10.7.4 while for the condition of a constant wall heat flux (\( q_w = \text{const.} \)) they are shown in Table 10.7.5.

Case: \( T_w = \text{constant} \)

Referring to the least error in the scatter of all experimental data the correlation proposed by [Notter and Sleicher, 1972] seems to fit best to all data for the case of a constant wall temperature. The computational work and dimensional analysis in the late seventies performed by [Leslie, 1977] and numerical calculations by [El-Hadidy, et al., 1982] yield that there are no different exponents regarding the Reynolds and the Prandtl number. Their main result is that for \( T_w = \text{const.} \) the Nusselt
number is proportional to $Nu-Pe^{0.8}$, which holds for $Pe > 2 \times 10^2$ and pure convective flow. For a long time it was difficult to calculate the heat transfer in a circular tube by means of a direct numerical simulation, because of the singularity at the ducts centreline. However, a transformation of the problem made it accessible for a DNS and [Yu, et al., 2001] showed a universal solution in principle valid for all Prandtl numbers. They tried to match their findings with the different wall heat fluxes and to derive a unique correlation. The following set of equations is recommended as the best choice for $Pr_t > Pr$, but is subject to possible significant improvement, because still some simplifications had to be applied to the DNS.

$$u_o^* = 3.2 \cdot \frac{227}{r^*} + \left( \frac{50}{r^*} \right)^2 + \frac{1}{0.436} \ln[r^*]$$

$$\frac{Nu - Nu(Pr = 0)}{Nu(Pr = Pr_t) - Nu(Pr = 0)} = \frac{1}{1 + \left( \frac{Pr_t}{Pr} \right)^{1/3}} \left( \frac{Nu(Pr = Pr_t, y = \infty)}{Nu(Pr = Pr_t)} \right) - \frac{2}{3} \frac{Nu(Pr = Pr_t)}{Nu(Pr = Pr_t)}$$

$$Nu(Pr = 0) = \frac{8}{1 + \frac{1.540}{(u_0^*)^{1.7}}}, \quad \text{and} \quad Nu(Pr = Pr_t) = \frac{Re(f/2)}{1 + \frac{145}{(u_0^*)^{2.2}}}$$

where $r^*$ is the dimensionless tube co-ordinate ($r^* = r/\left(\tau_{w} \rho \nu \right)^{1/2}$), and $u_0^*$ the dimensionless velocity normalised by $(v_0^* = u_0 \nu / \tau_{w})$, $Pr$ the molecular and $Pr_t$ the turbulent Prandtl number, $Re$ the Reynolds number and $f$ the (Fanning-) friction factor ($f = 2 \tau_{w}/(\rho u_0^2)$). According to their estimates on the error compared to the [Notter and Sleicher, 1972] correlation is reduced by more than 50%.

Although some simplifications and assumptions were introduced (for details see e.g. [Churchill, 2000 or Churchill, et al., 2000]) they found a good representation for all of the computed values of $Nu$ without the introduction of any explicit empiricism compared to other DNS calculations. In either event, a correlation for turbulent Prandtl number $Pr_t$ like the subsequent named ones (10.103)(a,b) is necessary to obtain numerical values of $Nu$ using a pocket computer. Also empirical expressions (from the DNS) such as the two equations (10.102)(c,d) are needed for $Nu = Nu(Pr = 0)$ and $Nu = Nu(Pr = Pr_t)$ for values of $r^*$ intermediate to or above those for which the computations were carried out by [Yu, et al., 2001].

$$Pr_t = \left[ 1 + \frac{10}{35 + \frac{(u \nu)}{1 - (u \nu)}} \right]^{-1}$$

$$\left( 1 + \frac{1}{\Phi} \right) \left( \frac{1}{0.025 Pr} \left( \frac{(u \nu)}{1 - (u \nu)} \right) + \Phi \right)$$

$$\Phi = 90 Pr^{-1/2} \left[ \frac{(u \nu)}{1 - (u \nu)} \right]$$

The later expression already appeared in the article by [Jischa and Rieke, 1979].
It is interesting to note in this context that the ratio of the wall Nusselt numbers for the constant wall temperature and the case of constant wall heat flux found in the DNS studies is nearly the same as the analytical result derived by [Tricoli, 1999], see Eq. (10.99). That means that the Nusselt numbers for a constant wall temperature are in any case lower than for a constant wall heat flux at least by this ratio for a fully thermally and hydrodynamically developed turbulent pipe flow.

### Table 10.7.4. Fully developed turbulent flow Nusselt numbers in a smooth circular duct for Pr < 0.1 with a constant wall temperature (Tw = const.) from experiments

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Correlation</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Gilliland, et al., 1951]</td>
<td>( Nu = 3.3 + 0.02 Pe^{0.18} )</td>
<td>( 0 \leq Pr \leq 0.1 ) and ( 10^4 \leq Re \leq 5 \times 10^6 ), rather speculative description of the boundary conditions.</td>
</tr>
<tr>
<td>[Sleicher and Tribus, 1957]</td>
<td>( Nu = 4.8 + 0.015 Re^{0.91} Pr^{1.21} )</td>
<td>( 0 \leq Pr \leq 0.1 ) and ( 10^4 \leq Re \leq 5 \times 10^6 ), the predictions are within a bandwidth of -33% and +19.5% of [Notter &amp; Sleicher, 1972].</td>
</tr>
<tr>
<td>[Hartnett and Irvine, 1957]</td>
<td>( Nu = Nu_{slug} + 0.015 Pe^{0.8} ) with ( Nu_{slug} = 5.78 ) assuming a slug velocity profile</td>
<td>( 0 \leq Pr \leq 0.1 ) and ( 10^4 \leq Re \leq 5 \times 10^6 ), the predictions are 40% below the [Notter &amp; Sleicher, 1972] correlation.</td>
</tr>
<tr>
<td>[Azer and Chao, 1961]</td>
<td>( Nu = 5 + 0.05 Re^{0.77} Pr^{1.02} )</td>
<td>( 0 \leq Pr \leq 0.1 ) and ( 10^4 \leq Re \leq 5 \times 10^6 ), the predictions are within +14.2% and -18.6% of the [Notter &amp; Sleicher, 1972] correlation.</td>
</tr>
<tr>
<td>[Notter and Sleicher, 1972]</td>
<td>( Nu = 4.8 + 0.0156 Re^{0.85} Pr^{0.93} )</td>
<td>( 0.004 \leq Pr \leq 0.1 ) and ( 10^4 \leq Re \leq 5 \times 10^6 ), the predictions are based on a numerical analysis and the minimum error of the cloud of experimental data.</td>
</tr>
<tr>
<td>[Chen and Chiou, 1981]</td>
<td>( Nu = 4.5 + 0.0156 Re^{0.85} Pr^{0.86} )</td>
<td>( 0 \leq Pr \leq 0.1 ) and ( 10^4 \leq Re \leq 5 \times 10^6 ), the predictions are within a bandwidth of +36% and -2% of [Notter &amp; Sleicher, 1972].</td>
</tr>
</tbody>
</table>

---

**Case: \( q_w \) = constant**

The fully developed Nusselt numbers computed from the [Notter and Sleicher, 1972] correlations covers a wide range of the Reynolds numbers and molecular Prandtl numbers with the smallest error to all experimental data currently available. [Heng, et al., 1998] conducted a numerical study for the constant heated fully developed circular tube case based on the models proposed by [Churchill, 1997a and b]. The integrals to be solved are rather complex and can not be used in the context of an engineering approach. However, the results obtained by [Heng, et al., 1998] almost coincide with the DNS of [Yu, et al., 2001]. The maximum deviation found occurs for small \( r^+ \), where [Heng, et al., 1998] underpredict the Nusselt number by 1.8%. Since the experimental data basis for the uniform wall heating is considerably larger than for the uniform wall temperature, the empirical correlation derived by [Notter and Sleicher, 1972] is recommended to fit best all experimental data available. The deviation to the DNS data and other numerical results is for its valid Reynolds number range within the range of +5% over-prediction of the mean \( Nu \).

All preceding heat transfer results pertain to uniform heat flux or uniform wall temperature around the tubes perimeter. The technically important problem of circumferentially varying but axially constant wall heat flux was solved by [Reynolds, 1963], [Sparrow and Lin, 1963] and [Gartner, et al., 1974]. To the best knowledge of the author the only available experimental data are available by [Black and Sparrow, 1967], unfortunately not for liquid metals. Nevertheless, the analysis by [Gartner,
is performed also low Prandtl number fluids. Assuming a cosine heat flux variation at a given cross-section of the duct, the local Nusselt number around the perimeter can be calculated by:

$$q_w(\varphi) = \bar{q} \left( 1 + b \cos \varphi \right)$$

yields

$$Nu(\varphi) = \frac{1 + b \cos \varphi}{1/\Nu + (2G/b) \cos \varphi}$$

(10.104)

where $\Nu$ is the value of the uniform wall heat flux, $\bar{q}$ the mean heat flux, $b$ a specified constant and $G$ the circumferential heat flux function calculated by [Gartner, 1974]. $G$ is unity for laminar flows for all Prandtl numbers. The tabulated values can be taken from Table 10.7.6.

### Table 10.7.5. Fully developed turbulent flow Nusselt numbers in a smooth circular duct for $Pr < 0.1$ with a constant wall heat flux ($q_w = \text{const.}$) from experiments

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Correlation</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Lyon, 1949, 1951]</td>
<td>$Nu = 5 + 0.025 Pe^{0.8}$</td>
<td>$0 \leq Pr \leq 0.1$ and $10^3 \leq Re \leq 5 \times 10^5$, the predictions are within $+33%$ and $-6.5%$ of [Notter &amp; Sleicher, 1972].</td>
</tr>
<tr>
<td>[Subbotin, et al., 1962]</td>
<td>$Nu = 0.625 Pe^{0.64}$</td>
<td>$0 \leq Pr \leq 0.1$ and $10^3 \leq Re \leq 5 \times 10^5$, significant underprediction of [Notter &amp; Sleicher, 1972] by $-43%$.</td>
</tr>
<tr>
<td>[Lubarski and Kaufman, 1955]</td>
<td>$Nu = 6.3 + 0.016 Re^{0.91} Pr^{1.21}$</td>
<td>$0 \leq Pr \leq 0.1$ and $10^3 \leq Re \leq 5 \times 10^5$, the predictions are within a bandwidth of $-32%$ and $+26%$ of [Notter &amp; Sleicher, 1972].</td>
</tr>
<tr>
<td>[Sleicher and Tribus, 1957]</td>
<td>$Nu = Nu_{\text{slug}} + 0.015 Pe^{0.8}$</td>
<td>$0 \leq Pr \leq 0.1$ and $10^3 \leq Re \leq 5 \times 10^5$, the predictions are $44%$ below the [Notter &amp; Sleicher, 1972] correlation</td>
</tr>
<tr>
<td>[Hartnett and Irvine, 1957]</td>
<td>$Nu = Nu_{\text{slug}} + 0.015 Pe^{0.8}$</td>
<td>$0 \leq Pr \leq 0.1$ and $10^3 \leq Re \leq 5 \times 10^5$, the predictions are $44%$ below the [Notter &amp; Sleicher, 1972] correlation</td>
</tr>
<tr>
<td>[Dwyer, 1963]</td>
<td>$Nu = 7 + 0.025 \frac{Re Pr \cdot 1.82 Re^{0.54}}{(\varepsilon_{m} / v)_{\text{max}}^{0.8}}$</td>
<td>$0 \leq Pr \leq 0.1$ and $10^3 \leq Re \leq 5 \times 10^5$, the predictions are within $+31%$ and $-6.5%$ of the [Notter &amp; Sleicher, 1972] correlation.</td>
</tr>
<tr>
<td>[Skupinski, et al., 1965]</td>
<td>$Nu = 4.82 + 0.0185 Pe^{0.827}$</td>
<td>$0 \leq Pr \leq 0.1$ and $10^3 \leq Re \leq 5 \times 10^5$, the predictions are within $+22%$ and $-18%$ of the [Notter &amp; Sleicher, 1972] correlation</td>
</tr>
<tr>
<td>[Notter and Sleicher, 1972]</td>
<td>$Nu = 6.3 + 0.0167 Re^{0.85} Pr^{0.93}$</td>
<td>$0.004 \leq Pr \leq 0.1$ and $10^3 \leq Re \leq 10^8$, the predictions are based on a numerical analysis and the minimum error of the cloud of experimental data</td>
</tr>
<tr>
<td>[Chen and Chiou, 1981]</td>
<td>$Nu = 5.6 + 0.0165 Re^{0.85} Pr^{0.86}$</td>
<td>$0 \leq Pr \leq 0.1$ and $10^3 \leq Re \leq 5 \times 10^5$, the predictions are within a bandwidth of $+34%$ and $-7%$ of [Notter &amp; Sleicher, 1972].</td>
</tr>
<tr>
<td>[Lee, 1983]</td>
<td>$Nu = 3.01 Re^{0.0833}$</td>
<td>$0.001 \leq Pr \leq 0.02$ and $5 \times 10^3 \leq Re \leq 10^3$, where its predictions are within $+25%$ and $-44%$ of [Notter &amp; Sleicher, 1972].</td>
</tr>
</tbody>
</table>
Table 10.7.6. Calculated circumferential heat flux function $G$ for the use in conjunction with Eq. (10.104) for a fully developed turbulent pipe flow with varying thermal boundary conditions as a function of the Reynolds and Prandtl number from [Gartner, et al., 1974]

<table>
<thead>
<tr>
<th>$Pr$</th>
<th>$Re = 10^4$</th>
<th>$Re = 3 \times 10^4$</th>
<th>$Re = 10^5$</th>
<th>$Re = 3 \times 10^5$</th>
<th>$Re = 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>0.001</td>
<td>0.9989</td>
<td>0.9937</td>
<td>0.9561</td>
<td>0.8059</td>
<td>0.4853</td>
</tr>
<tr>
<td>0.003</td>
<td>0.9929</td>
<td>0.9613</td>
<td>0.8005</td>
<td>0.5042</td>
<td>0.2300</td>
</tr>
<tr>
<td>0.01</td>
<td>0.9499</td>
<td>0.7915</td>
<td>0.4567</td>
<td>0.2185</td>
<td>0.0867</td>
</tr>
<tr>
<td>0.03</td>
<td>0.7794</td>
<td>0.4705</td>
<td>0.2055</td>
<td>0.0888</td>
<td>0.0336</td>
</tr>
</tbody>
</table>

b) Hydrodynamically developing turbulent flow

Several attempts have been made to solve the problem of turbulent flow development in a smooth circular duct starting with a uniform velocity profile at the ducts inlet. The closed form analytical solution of [Zhi-quing, 1982] is particularly suitable for engineering applications. According to this analysis the velocity distributions in the hydrodynamic entrance region is given by:

$$u_{max} = \begin{cases} 
(y/\delta)^{1/7} \text{ for } 0 \leq y < \delta \\
1 \text{ for } \delta \leq y \leq R
\end{cases} \quad \frac{u_0}{u_{max}} = 1 - \frac{1}{4} \left( \frac{\delta}{R} \right) + \frac{1}{15} \left( \frac{\delta}{R} \right)^2$$

where the hydrodynamic boundary layer thickness $\delta$, which varies with the axial co-ordinate $x$ in accordance with the relation:

$$\frac{x/d_h}{Re^{1/4}} = 1.4039 \left( \frac{\delta}{R} \right)^{3/2} \left[ 1 + 0.1577 \left( \frac{\delta}{R} \right) - 0.1793 \left( \frac{\delta}{R} \right)^{2} - 0.0168 \left( \frac{\delta}{R} \right)^3 + 0.0064 \left( \frac{\delta}{R} \right)^4 \right]$$

Although new DNS studies calculate the entrance length problem nearly exact for engineering purposes the following relation by [Zhi-quing, 1982] matches for a smooth circular duct the hydraulic developing length $l_{hy}/d_h$ quite well. The accuracy is around $\pm 10\%$. According to their proposal the developing length, defined as the axial distance at which the hydrodynamic boundary layer growing from the duct wall reaches the duct centreline, reads to:

$$\frac{l_{hy}}{d_h} = 1.3590 \cdot Re^{1/4}$$

(c) Thermally developing turbulent flow

The problem of a hydraulically developed and a thermally developing flow has been analytically, numerically and experimentally considered by many authors.

Case: $T_w = $ constant

For the case of a constant wall temperature this problem is often referred to as the turbulent Graetz problem. The first, who treated this problem considering liquid metals analytically where [Sleicher and Tribus, 1956]. [Notter and Sleicher, 1972] provided analytical solutions for numerous
Prandtl numbers in the range from $0 < Pr < 10^4$. All solutions presented are of infinite series type like in the laminar case. But, in contrast to the laminar flow the individual eigenvalues and constants are functions of the Reynolds and the Prandtl number.

Related to the analytical solutions the thermal entrance length $l_{th}$ can be calculated according to the solution of [Notter and Sleicher, 1972]. The deviation to newer numerical calculations performed by [Weigand, 1996] is of marginally nature ($<2\%$) except for Reynolds numbers less than $10^4$, where axial conduction becomes important. In this context the thermal entrance length is defined as the axial distance at which the local Nusselt number $Nu_x$ reaches 1.05 times the Nusselt number of the fully developed flow problem, i.e. $Nu_x = 1.05 Nu$. The calculated thermal entrance length as a function of the Reynolds number is displayed in Figure 10.7.4.a for various Prandtl numbers according to [Notter and Sleicher, 1972].

Certain correlations for the Nusselt numbers in the thermal entrance region of a smooth circular duct were developed by several authors. However, many of them were applicable to only to a limited range of the Reynolds number and the Prandtl number. A comprehensive study relevant for liquid metals was only performed by [Chen and Chiu, 1981]. They propose the following correlations for the local and the mean Nusselt numbers valid for $x/d_h$ and $Pe > 5\times10^2$:

$$\frac{Nu_x}{Nu_m} = 1 + \frac{2.4}{x/d_h} \left(\frac{1}{x/d_h}\right)^2$$

and

$$\frac{Nu_m}{Nu_m} = 1 + \frac{7}{x/d_h} + \frac{2.8}{\left(x/d_h\right)^2} \ln \left[\frac{x/d_h}{10}\right]$$

where $Nu_m$ is the Nusselt number of the fully developed flow. They recommend in this context the Notter-Sleicher-correlation with:

$$Nu_m = 4.5 + 0.0156 Re^{0.85} Pr^{0.86}$$

Case: $q_w = constant$

A similar approach was performed by [Becker, 1956] and was modified by [Genin, et al., 1978]. While the latter supported their analytical studies by several experiments they found that the local Nusselt number in the thermally developing flow can be calculated according to:

$$Nu_x = Nu_m + 0.006 \left(\frac{x/d_h}{Pe}\right)^{1.2}$$

with $Nu_m = 5.6 + 0.0165 Re^{0.85} Pr^{0.86}$

In a parametric study they show that their correlation is valid for $1.9\times10^2 < Pe < 1.8\times10^3$ with an accuracy of $\pm9\%$. The thermal entrance length corresponding to $Nu_x = 1.05 Nu_m$ was found to be best represented by their experimental data with the correlation:

$$\frac{l_{th}}{d_h} = \frac{Pe}{1 + 0.002 Pe}$$

[Lee, 1983] confirmed their studies and, moreover, he studied the effect of axial conduction on the solution for constant wall heat flux. Similar to the previous authors he found, that the thermal developing length for a constant wall heat flux are larger than those for a constant wall temperature. The normalised thermal developing length $l_{th}/d_h$ as a function of the Reynolds number for a constant wall heat flux is depicted in Figure 10.7.4(b).
Figure 10.7.4. Normalised thermal developing length \( l_{th}/dh \) as a function of the Reynolds number in a hydraulically fully developed flow of a smooth circular tube for different Prandtl numbers from [Notter and Sleicher, 1972]

\[ \text{a) } T_w = \text{constant, b) } q_w = \text{constant} \]

\[ \text{d) Simultaneously developing turbulent flow} \]

The simultaneously turbulent flow in a smooth duct is affected appreciably by the type of duct entrance configuration. [Boelter, et al., 1948] and [Mills, 1962] conducted an extensive experimental study for various inlet configurations into a smooth circular duct. While the first employed a constant wall temperature the latter performed a series for a constant wall heat flux. As a result of all these measurements it turned out that the measured local Nusselt numbers are substantially larger than that of thermally developing flow (at hydraulically developed flow), underscoring the decisive role played by the duct entrance configuration. Especially, the square inlet region for \( x/d_h < 2 \) exhibits a strange Nusselt number distribution with a steep increase and then a rapid drop for \( x/d_h > 2 \), which is apparently caused by the flow contraction followed by the re-expansion in the vicinity of the duct inlet. While for liquids with \( Pr \geq 0.72 \) Sparrow and co-workers ([Sparrow, et al., 1980], [Sparrow and O’Brien, 1980], [Sparrow and Gurdal, 1981], [Sparrow, et al., 1981], [Sparrow and Chaboki, 1984], [Lau, et al., 1981], [Sparrow and Bosmans, 1983], [Wesley and Sparrow, 1976] and [Molki and Sparrow, 1983]) performed extensive semi-analytical and experimental studies the data basis and the experimental verification for liquid metals is rather sparse. [Chen and Chiou, 1981] presented correlations for the simultaneously developing flow of liquid metals in a smooth circular duct with uniform velocity profile at the inlet. The correlations for the local Nusselt number \( Nu_x \) valid for \( 2 \leq x/d_h \leq 35, Pe > 5 \times 10^2 \) and \( Pr \leq 0.03 \) are given by:

\[
\begin{align*}
\frac{Nu_x}{Nu_m} &= 0.88 + \frac{2.4}{x/d_h} - \frac{1.25}{(x/d_h)^2} - A, \\
\frac{Nu_x}{Nu_m} &= 1 + \frac{5}{x/d_h} + \frac{1.86}{(x/d_h)^2} \ln\left(\frac{x/d_h}{10}\right) - B
\end{align*}
\]

where for a constant wall temperature \( (T_w = \text{const.}) \) the constants \( A \) and \( B \) read to:

\[
A = \frac{40 - x/d_h}{190}, \quad B = 0.09
\]

while for constant wall heat flux \( (q_w = \text{const.}) \) \( A \) and \( B \) vanish to zero.
Turbulent heat transfer in a flat duct

The flat duct heat transfer problem has been studied quite extensively by many authors in the past as this type of duct constitutes the limiting geometry for the family of rectangular and concentric annular ducts. In this context a duct is considered to be flat if its height \((2a)\) to width \((2b)\) ratio is smaller than 0.1, i.e. \(ab \leq 0.1\).

a) Fully developed flow

[Kays and Leung, 1963] presented comprehensive turbulent heat transfer results for arbitrarily prescribed heat fluxes at the two duct walls. Based on their analysis, the fully developed Nusselt number for the constant wall heat flux case can be represented from:

\[ Nu_{\text{const } q} = \frac{Nu}{1 - \gamma \varphi} \]  

(10.112)

where \(\gamma\) is the ratio of the prescribed heat fluxes at the two duct walls, i.e. for \(\gamma = 0\) one wall is heated and the other adiabatic, for \(\gamma = 1\) both are heated with the same heat flux and \(\gamma = -1\) one is heated and the other cooled with the same rate. The Nusselt number \(Nu\) and the influence coefficient \(\varphi\) entering Eq. (10.112) can be taken from Table 10.7.7 for the case of \(\gamma = 0\).

### Table 10.7.7. Nusselt numbers and influence coefficients for fully developed turbulent flow in a smooth flat duct with uniform heat flux at one wall and the other adiabatic \((\gamma = 0)\) from [Kays and Leung, 1963]

<table>
<thead>
<tr>
<th>Pr</th>
<th>(Re = 10^3)</th>
<th>(Re = 3 \times 10^4)</th>
<th>(Re = 10^5)</th>
<th>(Re = 3 \times 10^5)</th>
<th>(Re = 10^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Nu)</td>
<td>(\varphi)</td>
<td>(Nu)</td>
<td>(\varphi)</td>
<td>(Nu)</td>
</tr>
<tr>
<td>0</td>
<td>5.7</td>
<td>0.428</td>
<td>5.78</td>
<td>0.445</td>
<td>5.80</td>
</tr>
<tr>
<td>0.001</td>
<td>5.7</td>
<td>0.428</td>
<td>5.78</td>
<td>0.445</td>
<td>5.80</td>
</tr>
<tr>
<td>0.003</td>
<td>5.7</td>
<td>0.428</td>
<td>5.80</td>
<td>0.445</td>
<td>5.90</td>
</tr>
<tr>
<td>0.01</td>
<td>5.8</td>
<td>0.428</td>
<td>5.92</td>
<td>0.445</td>
<td>6.70</td>
</tr>
<tr>
<td>0.03</td>
<td>6.1</td>
<td>0.428</td>
<td>6.90</td>
<td>0.428</td>
<td>11.00</td>
</tr>
</tbody>
</table>

In order to verify whether the \(Nu\) predictions can be derived from the circular duct correlations, the predictions of the Eq. (10.112) are compared to the Notter-Sleicher-correlation in Table 10.7.5. Comparing the calculated data and building the ratio \(Nu_{\text{flat duct}}/Nu_{\text{pipe}}\) this ratio varies from +1.57 to -1.055 in the Reynolds number range \(10^4 < Re < 10^6\). Similar to the results for the circular duct, it is found that the Nusselt numbers in a flat duct for a constant wall heat flux are lower than for a constant wall heat flux. Certain empirical correlations are developed to calculate the fully developed heat transfer in a smooth flat duct for different boundary conditions. For \(\gamma = 0\) (one wall is heated and the other adiabatic) three correlations are available, one presented by [Buleev, 1959], [Dwyer, 1965] and [Duchatelle and Vautrey, 1964]. They read to:

\[ Nu_{\text{const } q} = 5.1 + 0.02 Pe^{0.8} \]  

(10.113)

\[ Nu_{\text{const } q} = 5.6 + 0.01905 Pe^{0.75} \]  

\[ Nu_{\text{const } q} = 5.85 + 0.000341 Pe^{1.29} \]
All these correlations are claimed to be valid for $0 \leq Pr \leq 0.004$ and $10^4 \leq Re \leq 10^5$. The latter expression derived by [Duchatelle and Vautrey, 1965] matches the analytic result obtained by [Kays and Leung, 1963] with an accuracy of $+24\%$ to $-11\%$ best for $\gamma = 0$ and is thus recommend for use. Many newer DNS calculations (see [Kasagi and Otsubo, 1993] or [Kawamura, 1995]) show that the Nusselt number varies only marginally with increasing Peclet number up to $Pe \sim 3 \times 10^5$. The only experiment matching this finding within an accuracy of $\pm 6\%$ is the Duchatelle and Vautrey experiment.

[Dwyer, 1965] presented the following empirical correlation for both walls heated ($\gamma = 1$):

$$Nu_{(q_w=const)} = 9.49 + 0.0596Pe^{0.688}$$  \hspace{2cm} (10.114)  

(a)

DNS results from [Lyons, et al., 1993] and [Kim and Moin, 1989] considering a similar problem, however, show that the Dwyer correlation yields too optimistic Nusselt numbers (about $20\%$ larger than the DNS values). A detailed analysis performed by [Kawamura, et al., 1998] shows that the correlation derived by [Sleicher and Rouse, 1975] matches the experimental results for $\gamma = 1$ best.

For the case of a constant wall temperature with $\gamma = 0$ (one wall is heated and the other adiabatic) only one relevant experiment is available, which was performed by [Seban, 1950]. It yields to the following correlation:

$$Nu_{(T_w=const)} = 5.8 + 0.02Pe^{0.8}$$  \hspace{2cm} (10.114)  

(b)

A critical review on the quality of this relation can not be given since DNS data for this specific case could not be found in literature. But the lower Nusselt number for the case of constant wall temperatures compared to constant wall heat flux looks quite sensible.

b) Thermally developing flow

The thermally developing turbulent flow in a flat duct with uniform and equal wall temperatures has been solved analytically by [Sakakibara and Endo, 1976] and by [Shibani and Özişik, 1977]. The solution can be expressed by a series expansion similar like for the laminar flow.

[Hatton and Quarmby, 1963] studied the problem with one part of the plates being at a constant temperature and the opposite being insulated. The type of solution corresponds to the ones mentioned above and is of series expansion type. [Hatton, et al., 1964] and [Sakakibara, 1982] presented semi-analytical solutions for the case with constant wall heat flux. [Faggiani and Gori, 1980] studied analytically the effect of axial fluid conduction on thermally developing flows in a Reynolds number range of $7.06 \times 10^3 \leq Re \leq 7.4 \times 10^4$ for Prandtl numbers $0.001 \leq Pr \leq 0.1$. They concluded that the influence of axial fluid conduction is to significantly reduce the Nusselt numbers in the thermal entrance region. This effect however occurs mainly at weakly turbulent flow ($Re \leq 10^4$) and for small $x/d_h < 5$. Unfortunately, in none of the analytical and semi-analytical solutions the order of magnitude for the thermal developing length $l_h$ is mentioned or a Nusselt number correlation for the thermal entrance region is developed in dependence on the Reynolds number and the Prandtl number. Moreover, to the knowledge of the authors no experimental verification or a direct numerical simulation calculation exists, which could give an estimate on the quality of the derived solutions.

c) Simultaneously developing flow

Also the information on the simultaneously developing turbulent flow between parallel plates is relatively sparse. Here, however, an experiment conducted by [Duchatelle and Vautrey, 1964], in which
the local Nusselt numbers have been measured exists. In their set-up one wall was insulated and to the opposite one a constant wall heat flux was supplied. Figure 10.7.5 shows that the ratio of the local Nussel number $N_u$, to the fully developed flow Nusselt number $\overline{Nu}$ attains unity at $Pe/(x/d_h) = 25$.

**Figure 10.7.5. Normalised local Nusselt number for simultaneously developing turbulent flow in a smooth flat duct for $Pr = 0.02$ with one wall heated and the other insulated from [Duchatelle and Vautrey, 1964]**

Thus the thermal entrance length $l_{th}$ for the simultaneously developing flow can be estimated to $l_{th}/d_h = Pe/25$. For the thermally developing but hydrodynamically developed flow these authors estimate a significantly smaller thermal entrance length, i.e. $l_{th}/d_h = Pe/80$.

### 10.7.5.4 Turbulent heat transfer in a rectangular duct

It is generally difficult to give engineering correlations for the heat transfer in rectangular ducts, since the attainable Nusselt numbers depend not only on the heat flux transferred to the fluid but also to the thermal boundary conditions for the wall, the symmetry, the shape of the corners with the associated secondary flow, the pre-conditioning of the flow and many other aspects. Thus, the correlations presented in this context can only be used as an assessment of the potential heat transfer capability in a rectangular duct. The correlations shown are far away to perform a detailed design of a heat transfer unit because of a lack of detailed experimental data or verification by a direct numerical simulation. The database for both of the latter named classes is rather sparse for liquid metals. For an estimate on the heat transfer capability of a specific geometrical set-up a CFD simulation is recommended. It can give a more detailed insight in the heat transfer mechanisms than the use of the subsequent correlations, even if rather rough models like the simple $k$-$\varepsilon$ model (with all the deficits mentioned in Subsection 10.7.4) are used in the simulation.

A simple correlation is available for estimating fully developed Nusselt numbers in turbulent flow of liquid metals in rectangular ducts either for a constant wall heat flux and a constant wall temperature. The correlation was derived by [Hartnett and Irvine, 1957] for a uniform velocity distribution (slug flow) and a pure molecular conduction heat transfer mechanism. This correlation is given by:

$$Nu = \frac{2}{3} \overline{Nu}_{\text{slug}} + 0.015 Pe^{0.8} \quad \text{with} \quad \begin{cases} \overline{Nu}_{\text{slug}} = 5.78 \quad \text{for} \quad T_w = \text{const.} \\ \overline{Nu}_{\text{slug}} = 8.00 \quad \text{for} \quad q_w = \text{const.} \end{cases}$$

\hspace{1cm} (10.115)
In case of thermally developing or simultaneously developing flows no analytical and hardly experimental data are available. There are some correlations on the “market”, which look quite inconsistent to the results obtained for the circular tube and the subsequently described concentric annulus problem.

10.7.5.5 Turbulent heat transfer in a concentric annulus

The flow in a concentric annulus like a rod in a circular tube is one of the most studied turbulent thermal heat transfer problems. Especially in context with nuclear systems, where typically circular fuel rods are placed with a specific arrangement, the concentric annulus is often considered as a solution of the single problem. There exist numerous possibilities of thermal boundary conditions for this problem and not all of them are covered by a correlation. Below a consistent representation to the circular duct flow is tried and we concentrate our focus only to concentric annuli.

a) Fully developed flow

[Rensen, 1981] measured the fully developed Nusselt numbers in a concentric annulus, with the inner wall subjected to a uniform heat flux and the outer to be thermally insulated. The radius ratio \( r^* \), which is defined as \( r^* = r_i/r_o \), where \( r_i \) is the radius of the inner annulus and \( r_o \), that of the outer one was in his experiment \( r^* = 0.5409 \). From the experiment conducted for sodium \((Pr \approx 0.005)\) in a Reynolds number regime from \( 6 \times 10^3 < Re < 6 \times 10^4 \) he obtained a Nusselt number correlation in the form:

\[
Nu = 5.75 + 0.022Pe^{0.8}
\]  

(10.116)

[Hartnett and Irvine, 1957] presented an analytic solution for liquid metals with small Prandtl numbers [see Eq. (10.115)], which requires the knowledge of the slug Nusselt numbers for the conditions of constant wall heat flux and constant wall temperature. The slug Nusselt numbers \( Nu_{slug} \) for these two cases are depicted in Figure 10.7.6(a). For the case where one wall is subjected to a uniform heat flux and the other is insulated, which is in literature often referred to as the fundamental solution of the second kind, the slug Nusselt numbers are shown in Figure 10.7.6(b).

Figure 10.7.6. Slug flow Nusselt numbers for smooth concentric annular ducts with (a) constant wall temperature and constant wall heat flux and (b) inner or outer wall heated and the other wall being adiabatic from [Hartnett and Irvine, 1957]
The prediction of Eq. (10.115) for \( r^* = 0.5409 \) in conjunction with Figure 10.7.6(b) for the case of the inner wall heated and the outer wall insulated are 32% lower than those of Eq. (10.116). Related to this specific experiment Eq. (10.116) is limited to be valid for \( 28 \leq Pe \leq 354 \).

[Dwyer, 1966] developed semi-empirical correlations for liquid metal flows with \( Pr < 0.03 \) in concentric annuli with one wall subjected to a uniform heat flux and the other wall insulated. For the case of the outer wall heated the equations read to:

\[
Nu = A_0 + B_0 \cdot (\beta Pe)^n \quad \text{with} \quad A_0 = 5.26 + \frac{0.05}{r^*} , B_0 = 0.01848 + \frac{0.003154}{r^*} \cdot \frac{0.0001333}{r^2} , \quad n = 0.78 - \frac{0.01333}{r^*} + \frac{0.000833}{r^2} , \\
\beta = 1 - \frac{1.82}{Pr(\frac{\varepsilon_M}{\nu})_{max}^{1/4} } \quad \text{with} \quad \left( \frac{\varepsilon_M}{\nu} \right)_{max} = \frac{1}{2} \left( \frac{\varepsilon_M}{\nu} \right)_{max,core}
\]

An expression for \((\varepsilon_M/\nu)_{max,core}\) applicable to a circular duct \((r^* = 0)\) was developed by [Bhatti and Shah, 1987] which is \((\varepsilon_M/\nu)_{max,core} = 0.037 \, Re^{0.5}\), with \( f \) the Fanning friction factor. The agreement with the experimental data from [Petrovichev, 1959] is excellent. The data of [Baker and Sesonske, 1962] exhibit about 15% higher Nusselt numbers, however, an analysis of the data immediately exhibits that their flow was not fully developed. In the experiment by [Nimmo and Dwyer, 1966] the validity of the equations was extended to \( Pe \sim 3 \times 10^3 \).

For the case of the inner wall heated the [Dwyer, 1966] correlation read to:

\[
Nu = A_0 + B_0 \cdot (\beta Pe)^n \quad \text{with} \quad A_0 = 4.63 + \frac{0.686}{r^*} , B_0 = 0.02154 - \frac{0.000043}{r^*} , \quad n = 0.752 + \frac{0.01657}{r^*} - \frac{0.000883}{r^2}
\]

The equations in Eq. (10.118) demonstrated their validity in the Prandtl number range \(0.005 \leq Pr \leq 0.03\) for Peclet numbers \(3 \times 10^2 \leq Pe \leq 3 \times 10^3\). The accuracy in this range is about 10-15%.

The predictions of Eq. (10.117) for \( r^* = 1 \) are within \(+20\% \) and \(-13\% \) of the prediction of Eq. (10.113c) derived by [Duchatelle and Vautrey, 1965]. For Peclet numbers below \( Pe = 1.2 \times 10^3 \) the uncertainty level falls below 6%.

b) Thermally developing flow

[Quarmby and Anand, 1970] provided an eigenvalue solution for the concentric annuli problem for different \( r^* \) and Prandtl numbers covering the Reynolds number range \(2 \times 10^4 \leq Re \leq 2.4 \times 10^5\). This solution looks quite well for large Prandtl numbers but underestimated the data of [Rensen, 1981]

A detailed measurement of the thermal entrance length \( l_{th}/d_0 \) was only performed in the experimental studies by [Rensen, 1981]. In his set-up with the inner wall heated \( (q_w = \text{const.}) \) and the outer adiabatic he found for sodium \( (Pr = 0.0054) \) a strong dependence of the thermal entrance length on the Reynolds number, which is tabulated in Table 10.7.8. Here, a fully developed flow is established if the criterion \( Nu_{th} < 1.05 Nu \) is matched.
Table 10.7.8. Thermal entrance length \( l_{th}/d_h \) for thermally developing flow in a smooth concentric annulus with \( r^* = 0.5409 \) for sodium (\( Pr = 0.0054 \)) with the inner wall heated and the outer adiabatic after [Rensen, 1981]

<table>
<thead>
<tr>
<th>Re</th>
<th>( l_{th}/d_h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2 \times 10^3 ) (laminar)</td>
<td>80.0</td>
</tr>
<tr>
<td>( 6 \times 10^3 ) (laminar-turb. transition)</td>
<td>2.1</td>
</tr>
<tr>
<td>( 8 \times 10^3 )</td>
<td>2.7</td>
</tr>
<tr>
<td>( 1 \times 10^4 )</td>
<td>3.2</td>
</tr>
<tr>
<td>( 2 \times 10^4 )</td>
<td>6.0</td>
</tr>
<tr>
<td>( 5 \times 10^4 )</td>
<td>13.0</td>
</tr>
<tr>
<td>( 6 \times 10^4 )</td>
<td>13.5</td>
</tr>
</tbody>
</table>

c) Simultaneously developing flow

There appears to be little information available on simultaneously developing flow in concentric annuli. An integral analysis presented by [Roberts and Barrow, 1967] who also conducted an extensive experimental series found that the results are not very much different to those obtained for thermally developing flows with a hydrodynamically developed velocity profile.

10.7.5.6 Turbulent heat transfer over rod bundles

Since the sixties the adequate cooling performance of the fuel elements using liquid metals was a major issue for the feasibility of fast breeder reactors. Many experimental investigations were performed to study the heat transfer in turbulent flow through rod bundles. They can be classified locally into three regions, the United States, the European Union and the former USSR. Without complaining completeness, numerous experimental heat transfer correlations have been developed, which are valid in a wide range of geometrical, thermal and flow boundary conditions in the following papers: [Subbotin, et al., 1961, 1964, 1967, 1970], [Friedland, et al., 1961a, b], [Borishanskii and Firsova, 1963 and 1964], [Maresca and Dwyer, 1964], [Nimmo and Dwyer, 1965], [Kalish and Dwyer, 1967], [Borishanskii, et al., 1967, 1969], [Pashek, 1967], [Hlavac, et al., 1969], [Zhukov, et al. 1969a, b, 1978, 1982], [Marchese, 1972], [Gräber and Rieger, 1973], [Weinberg, 1975], [Möller and Tschöke, 1978]. The comprehensive overview by [Weinberg, 1975] on the experimental studies exhibits that the correlations obtained are extremely sensitive to depositions of impurities on the surface, the question of the wetting especially to heavy liquid metals and the surface roughness. As one of his conclusions he mentioned that reliable correlations are only available for very few cases. One of the problems associated with the heat transfer over rod bundles is according to [Rehme, 1987] that only in a few experiments the temperatures are measured locally at different rods and that the temperature differences are often due to the high thermal conductivities of the liquid metals so small that reliable Nusselt number correlations are difficult to derive from these data.

Most of the experiments were performed in triangular or hexagonal arrays or bundles, which arise from the design intended to use or used in fast breeder reactors. The pitch (\( P \)) to pin (\( D \)) ratio, where \( P \) is the distance between the center of two neighbouring fuel rods and \( D \) is its diameter, ranges from \( 1.0 \leq P/D \leq 1.95 \) and the Peclet number from \( 2 \leq Pe \leq 4.5 \times 10^3 \). In this context rod bundles from 7 to 37 pins were investigated. Only one experiment is available in square arrays with 9 heated rods in a cluster of 25 by [Ushakov, et al., 1963]. The problem of the turbulent Prandtl number for the calculation of the Nusselt number has been already discussed in Subsection 10.7.4 in the context of the closure methods for the turbulent heat flux.
For the liquid metal heat transfer in rod bundles and the case of vanishing Prandtl number [Zhukov, et al., 1973] and [Ushakov, et al., 1974] derived a general correlation. This correlation was first published by [Subbotin, et al., 1975] and extensions were reported by [Ushakov, et al., 1976, 1977 and 1979]. This general correlation was checked against numerous results, both experimental data and theoretical predictions and can be recommended for rod bundles arranged in a triangular or hexagonal arrangement and reads to:

\[
Nu = Nu_{\text{lam}} + \frac{3.67}{90(P/D)^2} \left[ 1 - \frac{1}{6} \left( \frac{P}{D} \right)^{30} - 1 - \sqrt{1.24 \varepsilon_K + 1.15} \right] \cdot Pe^{m_i} \tag{10.119}
\]

with \( m_i = 0.56 + 0.19 \frac{P}{D} - 0.1 \left( \frac{P}{D} \right)^{0.1} \) and

\[
Nu_{\text{lam}} = \left( 7.55 - \frac{6.3}{(P/D)} \right) \left( \frac{3.6P/D}{(P/D)^{30} + 2.5(\varepsilon_K^{0.36} + 3.2)} \right) \tag{10.120}
\]

The laminar Nusselt number \( Nu_{\text{lam}} \) was originally proposed by [Subbotin, 1974]. The thermal modelling parameter \( \varepsilon_K \) takes into account the effects of heat conduction in the fuel (\( \lambda_1 \)), the cladding (\( \lambda_2 \)) and the fluid (\( \lambda_3 \)) and can be estimated by:

\[
\varepsilon_K = \frac{\lambda_2}{\lambda_3} \left( 1 - \Lambda_0 \frac{r_2}{r_1} \right) \quad \text{with} \quad \Lambda_0 = \frac{\lambda_2 - \lambda_1}{\lambda_2 + \lambda_1} \tag{10.120}
\]

where \( r_1 \) and \( r_2 \) denotes the distances of the fuel rod rows from the centre of the bundle. The limiting case of \( \varepsilon_K \) are 0.01 for peripherally constant heat flux and infinity for peripherally constant temperature. Eq. (10.119) is valid in the ranges from 1.0 \( \leq P/D \leq 2.0 \) and the Peclet number from 1 \( \leq Pe \leq 4 \times 10^3 \) and 0.01 \( \leq \varepsilon_K < \infty \). In Figure 10.7.7 the Nusselt number calculated after Eq. (10.119) is shown as a function of the Peclet number for different \( P/D \).

**Figure 10.7.7. Nusselt numbers in fully developed flow in rod bundles arranged in a triangular array as a function of the Peclet number \( Pe \) and \( P/D \) for constant wall heat flux**

![Graph showing Nusselt numbers as a function of Pe and P/D](image-url)
In case $P/D$ grows beyond 1.3 the effect of $\varepsilon_k$ diminishes and Eq. (10.119) reduces to:

$$Nu = 7.55 \frac{P}{D} - 20 \left( \frac{P}{D} \right)^{13} + \frac{3.67}{90(P/D)} Pe^{0.19(P/D)-0.56} \quad (10.121)$$

It is valid for $1.0 \leq P/D \leq 2.0$ and from $1 \leq Pe \leq 4 \times 10^3$. The thermal hydraulic design is usually performed by subchannel codes, which compute fluid and surface temperatures averaged over each subchannel. Therefore, it is important to know the peripheral variations of the rod surface temperatures superimposed on the average temperature. The dimensionless peripheral variation of the surface temperature is correlated by [Subbotin, 1974 and 1975] and [Ushakov, 1979] and reads to Eq. (10.122).

$$\Delta T_{\text{max}, \text{lam}} = \frac{\Delta T_{\text{max}, \text{lam}}}{1 + \gamma Pe^\beta} \quad \text{with}$$

$$\gamma = 0.008(1 + 0.03\varepsilon_k) \quad \text{and} \quad \beta = 0.65 + \frac{51 \cdot \log_{10}(P/D)}{(P/D)^{20}},$$

$$\Delta T_{\text{max}} = 2k \frac{T_{\text{w}}^\text{max} - T_{\text{w}}^\text{min}}{q_w D} \quad \text{and}$$

$$\Delta T_{\text{max}, \text{lam}} = \frac{0.022}{(P/D)^{(P/D-1)^{0.4}}} - 0.99 \left[ 1 - \tanh \left( \frac{1.2\exp(-26.4(P/D-1)) + 1.2\varepsilon_k}{0.84 + 0.2(P/D-1.06)^2} \right) \right]$$

In case of thermally developing flows along rod bundles the Nusselt number values may significantly deviate from the circular duct because of the strong geometric non-uniformity of the subchannels. If the coolant area per rod is taken to define an equivalent annulus with zero shear at its outer boundary, it is found that the Nusselt number predictions are accurate within $\pm 10\%$ for $P/D \geq 1.12$, see e.g. [Nijsing, 1972]. Especially, the entrance region is problematic since the entrance length is sensitive to $Re$, $Pr$ and the geometry. For a hydraulically fully developed flow only one experiment is available by [Subbotin, 1975], where he detected that fully developed thermal conditions in sodium could not be reached for $l_\text{th}/d_h$ below 200 (!) for $Pe > 10^5$. Their experimental data were obtained for a $P/D = 1.15$. For lower $P/D$ ratios the thermal developing length is even larger, because the heat transfer between the subchannels is reduced. This has been confirmed by the measurement of [Möller and Tschöke, 1980] obtained in a 19-rod bundle with $P/D = 1.31$. For a corner subchannel and $Pe = 150$ a thermal entrance length of $l_\text{th}/d_h = 70$ was measured. The use of fins reduces the thermal entrance length considerably, since it leads to a better lateral mixing. In the textbook by [Stasiulevivius and Skrinska, 1988] different options for fins on the rods are discussed and optimisation guidelines are given.
10.8 Some final remarks

This report mainly focuses on the forced convective single phase heat transfer of liquid metals in smooth ducts. Although the author is aware that in many technical applications this rather idealised case will hardly appear. Thus, this chapter requires in the future an extension to the heat transfer appearing in mixed and purely buoyancy governed flows.

A few aspects also need a closer view in context with all kinds of heat transfer in liquid metals. In recent years, many papers addressed the question of wetting and the influence of surface roughness, which is sometimes taken as an explanation for a mismatch of data. Although many experimenters spend a lot of effort to avoid this issue, it obviously leads to severe effects in thermal-hydraulic components and as a consequence to lower Nusselt numbers. But, the data basis for a closed discussion on these two topics seemed to me too sparse either theoretically and experimentally to dedicate an individual chapter to it. The nature of this chapter based only on the experimental results would be rather of speculative nature.

A topic also not considered up to now is the flow and the heat transfer around obstacles, which occurs in many reactor and metal refinement processes. Although here a much broader data basis is available it is difficult to structure this rather complex context in a short paragraph. But since it is important for the experimental investigation of heat transport phenomena it should be integrated in a next step of the liquid metal handbook.

Many advanced reactor concepts make use of the gas lift principle by means of a convection enhancement injecting gas into the heavy liquid metal. The resulting two-phase flow is theoretically difficult to describe due to the large density differences and currently only limited accessible to the modelling. Nevertheless, also here a large variety of experiments exist, which were performed in the context of the specific technical configuration used for the individual technical application. Associated with the two-phase flow problem is the treatment of free liquid metal surfaces, as they may appear in free surface targets of accelerator driven systems or other metallurgical processes. Here, mainly turbulent flows appear and currently a lot of effort is spent on the modelling of these free surfaces. The next issue of the liquid metal should contain a chapter dedicated only to this problem.
REFERENCES


Chapter 11
INSTRUMENTATION*

11.1 Background of the measurement technique development

Accelerator-driven systems (ADS) using lead (Pb) or eutectic lead-bismuth (PbBi) alloys require measurement technologies especially adapted to them. Besides their relatively high density, corrosivity, opaqueness, weak specific electric and thermal conductivity the sensors being in contact with the liquid are facing elevated temperatures in the range from 200°C to 550°C or even more. Although in the past decades a lot of progress has been achieved in developing liquid metal adapted measurement devices in the context of sodium operated fast breeder reactors only part of the knowledge can be transferred to lead or lead alloy cooled systems because of its specific properties.

While using measurement devices one must clearly distinguish between operational and maintenance purposes and scientific ones. A list of topics for the different requirement profiles are given in Table 11.1.1.

Table 11.1.1. Requirement profiles of measurement technologies for reactor and scientific purposes

<table>
<thead>
<tr>
<th>Maintenance and operation</th>
<th>Scientific use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reliable component and reactor operation</td>
<td>High spatial and temporal resolution</td>
</tr>
<tr>
<td>Safe system monitoring</td>
<td>Negligible impact on desired measurement effect</td>
</tr>
<tr>
<td>Sufficiently fast response time to abnormal conditions (shutdown)</td>
<td>Applicability in the specific environment (temperature, pressure magnetic fields, etc.)</td>
</tr>
<tr>
<td>Long life time</td>
<td>Repeatability and accuracy</td>
</tr>
<tr>
<td>Simple replacement</td>
<td>Calibration effort</td>
</tr>
<tr>
<td>Absolute value (no calibration required)</td>
<td></td>
</tr>
<tr>
<td>Reasonable price and accuracy</td>
<td></td>
</tr>
</tbody>
</table>

Fluid mechanical measurement devices are in principle divided into two classes of systems. One is the measurement of global quantities, which are mostly scalars like the flow rate, the pressure in the system or the mean temperatures. This class of devices is dedicated to reactor applications and the use in liquid metal loop operation. The other class is formed by measurement of local quantities like the velocity and void distribution, the heat flux, the surface structure and shape, which is necessary to capture effects occurring in generic scientific problems. The detection of these particular effects in benchmark problems allows the development of new physical models or the validation computational fluid dynamic (CFD) simulations. Naturally, the border between the two classes is not sharply defined. For instance by miniaturisation of pressure measurement devices Pitot or Prandtl tube can be developed able to detect smallest velocities.

* Chapter lead: Robert Stieglitz (FZK, Germany). The author would like to thank colleagues from the Karlsruhe Lead Laboratory (KALLA), the NUKLEAR programme at the Karlsruhe research centre, and many other unnamed persons for supplying information on this compression.
Of course, this handbook cannot cover the whole branch of measurement devices currently available or being under development. In this context we limit ourselves on the presentation of pressure and flow rate measurement devices, discuss some temperature measurement technologies and typical mistakes often made as well methodologies to measure local velocity and void fraction distributions, surface structures and liquid level detection techniques. For the individual devices the physical operation principles are explained, and often an example for the application in heavy liquid metals is described as well as an appropriate literature source is cited. As far as known to the authors the advantages and disadvantages are mentioned and discussed.

This chapter discusses instruments commonly used to measure process variables, with emphasis on instrument problems and on the types of instruments, primarily the sensors, peculiar to liquid metal applications. Some techniques established in the broader field of process-variable measurement and in other areas of instrumentation may be applicable, but because of the limited usage or apparent suitability in liquid metals, they are not discussed here. Since the instrumentation technology for lead and its alloys is still in its infancy, often examples for the application of specific techniques in other heavy liquid metals described which offer a potential transferability to lead and its systems. Among the quite broad amount instrumentation literature textbooks there are only a few related to liquid metal such as [Drowden, 1972] or [Foust, 1978]. In the context of the liquid metal handbook all data are expressed in metric units using the MKS system.

11.2 Flow meters

Many physical principles can be used to determine the flow rate of fluids in pipes [Goldstein, 1983], but the physical and chemical properties of lead bismuth exclude some of them right from the start. The opaqueness, which all liquid metals have in common, disables all optical methods, not only for a quantitative but also for a qualitative access to the flow. A review of liquid metal measurement techniques applied in the casting industry gives the overview article by [Argyropoulos, 2001]. In the following sections, the physical principles of the investigated methods are described.

11.2.1 Electromagnetic flow meters

11.2.1.1 DC electromagnetic flow meters

Permanent magnet flow meters (PMF) are mostly used if the installation volume is rather small or where low flow rates have to be resolved. According to the Faraday law an electrically conducting fluid flowing perpendicular to a magnetic field induces an electric field. The strength of this electric field is proportional to the flow velocity and can be measured with diametrically opposed electrodes on the pipe walls perpendicular to flow direction and magnetic field. A compilation of the theoretical concepts concerning electromagnetic flow measurements is given by the book of [Shercliff, 1962]. From the Maxwell equations the Poisson equation for an electromagnetic flow meter can be derived:

$$\nabla^2 \phi = \nabla \cdot (u \times B)$$  \hspace{1cm} (11.1)

with the electric potential $\phi$ and the vector quantities velocity $u$ and magnetic field $B$. The partial differential Eq. (11.1) cannot be solved in general, but with simplified boundary conditions and with the aid of the Green function a transformation can be made and a solution can be given for a finite region of a flow meter with point electrodes. For the voltage at the electrodes, derived from the electric potential difference $\Delta \phi$, one obtains with a weighting vector $W$, which indicates the contribution of the flow in a single volumetric element to the effective measurable voltage:
For an axially symmetric flow profile and an infinite, homogenous magnetic field follows the simple dependency:

$$\Delta \phi = \int_{x,y,z} W(u \times B)\,dx\,dy\,dz$$

(11.2)

showing the proportionality between the measured electrode voltage $\Delta \phi$ and the mean flow velocity $u_m$ depending on the mean magnetic field strength $B$ and the pipe diameter $d$. The weighting vector introduced in Eq. (11.2) was evaluated by [Shercliff, 1962, 1987] for an infinite long, homogeneous magnetic flow-meter field (2-D problem).

**Potential error sources of the PMF sensor and the correct installation**

With the weighting distribution shown in Figure 11.2.1 the influence of an asymmetric flow profile on the measurement accuracy of an electromagnetic flow meter can be estimated. Due to higher gradients in the weighting field, the use of point electrodes should introduce higher uncertainties in magnetic flow meter systems than line electrodes. In reality this can be observed, but the deviations are always small compared to the signal amplitude, normally lower than 1% [Bonfig, 2002]. A different situation occurs, when impurities accumulate in the near vicinity of the electrodes. In this case a massive change of the signal voltage arises and destroys the linearity of the flow meter system. Hence, Eq. (11.3) no longer holds and the flow meter becomes useless.

Figure 11.2.1. Evaluation of the weighting vector function based on [Shercliff, 1962] for (a) point electrodes and (b) line electrodes

Furthermore, the pipe walls at the electrodes and the fluid are forming a galvanic element, which produces an additional voltage depending on temperature, flow, pressure, the chemical properties of the fluid and the surface conditions of the steel walls. Consequently this voltage is different at both electrodes and contributes as a theoretically not calculable perturbation to the signal and has to be compensated by means of a calibration.

One problem is the variability of the boundary conditions while operation, which makes this calibration necessary in regular intervals. In particular, the non-definite wetting behaviour of liquid lead-bismuth to the electrically conducting structure material can lead to incorrect readings even during
one measurement day. The fluid may be wetted through the wall in the adhesive sense, so that the pressure drop in the piping shows a wetting of the surface. However, a contact resistance between the wall and the fluid may still exist. Due to this contact resistance part of the current induced in the fluid by the permanent magnetic field $B$ short-circuits in the fluid and the other one in the duct walls. This effect is important since the specific electric conductivity of liquid metals $\sigma_{LM}$ like lead or the eutectic alloy Pb$^{45}$Bi$^{55}$ is of the same order as that of the most structure materials like steel $\sigma_{wall}$, while for the use in sodium or sodium potassium most of the current is confined to the liquid, because there $\sigma_{LM}/\sigma_{wall} \gg 1$.

A last issue to the use of PMF and its set-up in piping systems should be mentioned. Since large permanent magnets covering the whole ducts cross-section, in which the flow rate is measured are expensive mostly misreadings appear especially at low flow rates. If the flow is laminar in the duct and the magnetic field is penetrating only a part of the cross-section, the non-homogeneous magnetic field modifies the laminar flow profile establishing in the duct. This leads to induction of smaller electric potentials transverse to the mean magnetic field und thus to an underestimation of the flow rate. This non-linearity at low flow velocities has to be considered by means of a Reynolds number analysis and can be taken into account by inserting Venturi nozzles upstream the PMF.

If the applied magnetic field is disturbed by another steady magnetic field the magnetic field lines are bended, see Figure 11.2.2(b). As a result the flow rate measured is not correct any more. However, if a magnetic shield in form of a ferromagnetic plate (with a high magnetic permeability $\mu_r \gg 1$) is placed between the flow meter and the scattering field the field lines of the scattering field are focused in the plate and hence the measurement field remains unchanged, see Figure 11.2.2(c). The thickness of the plate can be calculated using the magnetic potential equation. In general a few millimetres are enough to compensate a field of nearly one Tesla. The shown method of magnetic shielding works only for DC magnetic fields. In case of AC fields the flow meter has to be fully capsuled with ferro-magnetic materials.

**Figure 11.2.2.** (a) Measurement principle of a DC electromagnetic flow meter. (b) Influence of a scattering magnetic field on the magnetic field of a permanent electromagnetic flow meter. (c) Protection of the electromagnetic flow meter from a DC magnetic scattering field using a ferro-magnetic shielding.

Figure 11.2.3 shows a typical calibration curve of the electromagnetic flow meter in the THESYS technology loop of the KALLA laboratory [Knebel, et al., 2003]. There is a perfect linear relationship between induced potential and power supply to the pump. Due to the temperature dependence of the magnetic field, such a calibration has to be done for each operating temperature of the magnet.
Figure 11.2.3. Calibration curve of the DC electromagnetic flow meter (measured DC voltage as a function of the pump supply current) in the technology loop THESYS. Here the induced potential PMF is shown as a function of the pump power.

Operational characteristics

Figure 11.2.3 shows the normalised PMF signal plotted against temperature. Here, a clear linear dependency is observed for the four selected pump power stages. The slope of the four lines obviously varies linearly with the flow rate. Since a linear dependency between flow rate and PMF signal is expected, one can construct a linear equation with temperature depended slope:

$$V(U_{PMF}) = \frac{U_{PMF} - b}{m_T \cdot T + c}$$  \hspace{1cm} (11.4)

In Eq. (11.4) $V$ is the flow rate, $U_{PMF}$ the PMF signal, $T$ the temperature, $m_T$ the temperature dependent slope (sensitivity) of the PMF and $b$ and $c$ temperature depending offsets, which will be determined from the calibration against the heat balance. From the change of the slope of the lines in figure $m_T$ can be calculated and Eq. (11.4) gives the flow rate for a measured PMF signal.

On the left side of Figure 11.2.4 the results of the temperature correction is plotted in terms of the calculated flow rate against the pump power. From an error propagation analysis the uncertainty is calculated to 2% at a linear regression coefficient of 99.84%. The disadvantage of this method is the necessity of measurements at every point in the whole parameter range of flow rate and temperature to conduct the described calibration. This is a great effort and an isothermal operation is recommended, because this would require only two calibration measurements.

There is another argument against a protracted calibration process: the instable long-term behaviour of the investigated PMF systems in lead-bismuth. In the section of the PMF signal time series on the right side in Figure 11.2.4 an example for the observed discontinuities is shown. The jumps in the signal, which was taken at constant flow rate, can easily reach 20 times of the actual value. These annoyances are produced by galvanic reaction at the interface between pipe wall and liquid metal close to the electrodes and are worsened by accumulating impurities at these positions. Additionally, the corrosion of the pipe material (liquid metal corrosion and/or oxidation) changes the liquid-solid interface properties and causes a drift of the PMF signal. A favourable positioning and the use of line electrodes can work against these problems, but a recalibration in regular intervals is still necessary.
11.2.1.2 AC electromagnetic flow meter (EMFM)

A possibility using electromagnetic effects to measure the flow rate which suffers not from these problems is the electromagnetic frequency flow meter (EMFM). The general measurement principle of such an induction flow meter is that the motion of an electrically conducting fluid in an imposed field $B$ produces an induced field $B'$ which is proportional to the flow rate in the first order. This method involves an effect which is proportional to the fluid conductivity $\sigma$. Indeed, if the fluid velocity is known this method has been used to measure the conductivity of ionised gases [Lin, et al., 1955]. The attraction of the EMFM is that its indication is directly electrical and no transducer is required which allows a large temporal resolution. Moreover, for the acquisition no direct contact of the sensor with the operation fluid is necessary, so that material compatibility issues play a role.

The earliest proposal for an EMFM has been made by [Lehde and Lang, 1948], which scheme is illustrated in Figure 11.2.5. The two coils $A$ and $C$ are energised in series-opposition so as to produce an AC magnetic field of the form illustrated in Figure 11.2.5 at the bottom. In the absence of a fluid motion the field is symmetrical and induces no signal in the sensing coil $B$ according to the induction equation. As soon as flow occurs, the magnetic field lines are dragged downstream by $(u\nabla B)$ and a signal appears in coil $B$, which is proportional to the flow rate to the first order. But great care is necessary that there is no output signal in case of zero flow and in practice it is hardly feasible to produce a geometrically exact symmetric arrangement. Thus a precise fabrication is required otherwise the genuine signal, which is quite often small, will be lost among stray signals.

The flow direction can be detected by the sign of the RMS value of the sensing coil. The magnitude of the RMS value in the sensing coil is proportional to the magnetic Reynolds number of the fluid flow $Re_m$, where $Re_m$ is calculated according to Eq. (11.5).

$$Re_m = \mu_0 \sigma(T) u_m d$$  \hspace{1cm} (11.5)

where $\mu_0$ is the magnetic permeability of vacuum, given as $4\pi \times 10^{-7}$ $\text{A} \cdot \text{s}/\text{V} \cdot \text{m}$, $\sigma$ the specific electric conductivity of the fluid as a function of the temperature $T$, $u_m$ the mean flow velocity within the duct and $d$ its diameter. The magnetic Reynolds number weights the induced magnetic field to the initially by the AC current applied magnetic field. If the temperature remains constant the measured RMS value of $\Delta \Phi$ is proportional to the mean fluid velocity $u_m$. 

484
Figure 11.2.5. Operation principle of an electromagnetic frequency flow meter (EMFM) freely adapted from [Lehde and Lang, 1948]

**Potential error sources of the PMF sensor and the correct installation**

However, this linear increase of the signal with the velocity and hence this operation principle only is valid if the magnetic Reynolds number $Re_m$ is significantly smaller than unity. Only then the induced potential $(u_m \times B)$ and the associated Lorentz-force $(j \times B)$ can be approximated by the $(u_m \times B_{\text{imposed}})$ and $(j \times B_{\text{imposed}})$. But, if $Re_m$ is of $O(1)$ the non-linear contributions $(u_m \times B_{\text{induced}})$ and $(j \times B_{\text{induced}})$ become important. Other non-linear behaviour will occur if the imposed magnetic field $B(t)$ is strong enough to perturb the flow pattern. This effect is expressed by the Hartmann number $Ha$ or $(M)$, which weights the electromagnetic forces versus the viscous ones, and the Stewart number $St$, (often called interaction parameter). The latter one can be confess as the ratio of the electromagnetic forces versus the inertial forces within the fluid. Both quantities are calculated according to Eq. (11.6). They must be smaller than unity [Shercliff, 1987] throughout the operation range of the electromagnetic induction flow meter.

\[
Ha = dB_{\text{max}} \sqrt{\frac{\sigma(T)}{\rho(T) \cdot v(T)}} \quad \text{and} \quad St = \frac{d\sigma(T)B_{\text{max}}^2}{\rho(T)u_m} \tag{11.6}
\]

In Eq. (11.6) $\rho$ is the fluid density, $B_{\text{max}}$ the peak magnetic induction and $v$ the kinematic viscosity of the fluid.
Also for the sensing coil counteracting demands exits. One the one hand a lot of wire turns are required in order to detect smallest flow rate changes without using sophisticated AC amplifiers. But, on the other hand the more wire turns the coil has the more enforced the problem of pick-up effects is. The pick-up effect is meant the occurrence of stray AC signals superimposed on the flow dependent signal. The main source of pick-up are stray alternating fields from nearby placed equipment, such as electromagnetic pumps and AC powered equipment like ventilators, personal computers, etc. They can never be suppressed entirely and a large effort has to be directed into separating the wanted from the stray signals. As a rule, separation of the signals is achieved by exploiting the fact that the flow dependent signal and the pick-up are in quadrature, the first being proportional to the magnetic field strength, and the second to its time-derivative [Davidson, 2001]. This calibration necessitates elaborate electronic equipment.

Another complication is caused by phase shifts due to eddy currents in nearby solid and fluid conductors, because of the generation of harmonics through the non-linearity of the material or because of capacitive pick-up. Another source of trouble can be resonance or beats when the flow contains slight periodic fluctuations due, for instance, the use of electromagnetic or mechanical pumps running at or near synchronous speed. A technically feasible solution to minimise pick-up effects is a complete enclosure of the EMFM device by means of a ferromagnetic foil, being thick enough to run not into saturation of external DC and AC magnetic fields. This foil has to be grounded through the liquid flow far away of any eddy currents.

Finally, also some limitations concerning the AC current feed \( j(t) \) have to be considered, which are also of contradictory nature. A minimisation of pick-up effects is achieved if a low frequency of \( j(t) \) is used but if it is necessary to study the instantaneous of transient or pulsating flows the frequency must be at least three times higher than the highest frequency of interest occurring in the flow. Also frequencies have to be omitted which are a factor of the environmental power supply in order to avoid the generation of sub- and super-harmonics in the sensing signal. Of course, also a definite upper limit of the acceptable frequency exists. If the fluid is a good conductor the frequency must not be so high as to cause a skin-effect, while if the fluid is a poor conductor the frequency \( \omega \), which is \( \omega = 2 \pi f \), must not be so high that dielectric relaxation is not virtually instantaneous. The condition for there to be no skin-effect is:

\[
\omega d^2 \mu \sigma(T) << 1
\]

and for immediate dielectric relaxation, which means a negligible displacement current, is given by:

\[
\frac{\omega \varepsilon \varepsilon_0}{\sigma(T)} << 1
\]

where \( \varepsilon \) is the permittivity of the fluid and \( \varepsilon_0 \) the electric field constant given by \( \varepsilon_0 = 8.85419 \times 10^{-12} \text{ As/V/m} \). In case of liquid metals the permittivity \( \varepsilon \) is closely over unity, i.e. 1.01 [Siemens, 1969].

A photograph of an EMFM flow meter taken during the fabrication (a) and its installation in the THESYS loop of KALLA (b) is shown in Figure 11.2.6. For the calculation of the magnetic peak induction Eq. (11.9) is used:

\[
B_{\text{max}} = \frac{I_{\text{max}} \cdot R}{n(Lf) \pi d_{\text{Coils},A}}
\]
where \( R \) is the ohmic resistance of the coils, \( L \) the coil width, \( n \) the number of current turns and \( d_{\text{m,Coils,A}} \) the mean diameter of the feeding coils. As long as the Stewart number and the magnetic Reynolds number are significantly lower than unity a linear behaviour of the flow meter with respect to the temperature can be expected. The linear dependence of the signal induced in a typical EMFM flow meter for heavy liquid metals as a function of the pumping power for a constant temperature of 300°C and different feeding currents and frequencies is shown in Figure 11.2.7.

An exact theoretical analysis of the EMFM is usually difficult and an empirical calibration for each device is inevitable.

**Figure 11.2.6.** (a) EMFM fabrication at the KALLA laboratory. (b) Installation of the EMFM in the technology loop THESYS of KALLA.

**Figure 11.2.7.** Measured EMFM signal as a function of the pumping power for different feeding currents and feeding frequencies of the pump at a constant temperature of \( T = 300°C \) in the THESYS loop of KALLA: Characteristics (left) and calculated flow rate (right).

**Operational characteristics**

For a frequency of 500 Hz an increase of the EMFM signal with higher feeding current is obvious, but there is hardly an effect at a frequency of 1 kHz. This is a clear indicator for the occurrence of the skin effect. The magnetic field can penetrate just a thin boundary layer where the fluid moves so slowly that a change of the induced field strength causes only a marginal change of the output signal.
Consequently the performance of the EMFM flow meter increases with lower frequency and the best is found for 100 mA feeding current at 500 Hz. Higher feeding currents are not feasible because the strong magnetic field would cause MHD effects which change the flow pattern.

To verify the linearity of the characteristic, the flow rate was calculated using the result of a heat balance at 100% pump power. The results are plotted against the pump power shown in the right diagram on Figure 11.2.7. All values are found to lie inside the 95% prediction limit of their linear regression regardless of the parameter used for the feeding current. If a reliable calibration can be made, the EMFM is a very stable and robust flow rate measurement device for lead-bismuth loops.

11.2.2 Momentum-based flow meters

11.2.2.1 Turbine flow meter

In a turbine flow meter the measuring element is an axial rotor, turned by the force generated by the flowing fluid pushing onto the turbine blades. In the most applications this rotation will be picked up by a magnetic sensing coil placed onto the housing in the immediate vicinity of the interiorly passing blades. The measured rotation frequency is direct proportional to the volumetric flow rate. In reality bearing friction and dependencies on the flow profile, the viscosity of the fluid and eddy production in the turbine cause a disturbance of the linear characteristics. These influences are compensated by means of integrated flow straighteners and factory calibrations with a model fluid of the same viscosity as the future working fluid. Turbine flow meters like that shown in Figure 11.2.8 are commercially available for different pipe diameters [Natec Schultheiß, 1999]. They are used for flow rate measurements of gases and turbulent flowing, low viscosity fluids and feature high measurement accuracy.

Figure 11.2.8. Construction sketch of a turbine flow meter [Natec Schultheiß, 1999]

For the application in liquid metals the question for compatible materials arises. Rotor and bearing have to withstand the corrosive environment and high temperature of the fluid. Because of their relatively wide conduit, turbines are rather unsusceptible to floating particles, but in heavy liquid metals impurities buoy upwards and can accumulate in the top region of the rotor housing. Hence, the narrow gap between rotor and housing can plug up and destroy the turbine.
An advantage of the turbine flow meter is the possibility to use it as a measurement standard, because its mechanical measurement principle depends only on a few very well known parameters and calibrations can be done with model fluids. Thus the turbine was selected for qualification in lead-bismuth flows.

Operational characteristics

For the tests of a turbine flow meter a device from the company Natec Schultheiß was purchased. The selected model FT-1600-YBBLED-6108 is a measurement turbine for liquids with a magnetic inductive pick-up system. Housing and rotor consist of stainless steel, journal, axis and bearing of carbide. As specified, fluid temperatures up to 600°C are allowed with this material combination, but the magnetic inductive pick-up has to be cooled [Natec Schultheiß, 1999]. The turbine was calibrated in a company laboratory with an oil mixture, which acts as a model for lead-bismuth at low temperature by adjusting its viscosity. Figure 11.2.9 shows a photograph of the used turbine flow meter and a view into its duct with the rotor.

Figure 11.2.9. Photographs of the Natec Schultheiß turbine flow meter installed in the THESYS loop of KALLA

To evaluate the performance of the turbine flow meter, a heat balance calibration was conducted like for the electromagnetic flow meters. Measurements were made at lead-bismuth temperatures from 200 to 250°C.

Figure 11.2.10 shows the flow rate as a function of pump power measured by means of the turbine flow meter in comparison with the values derived from the heat balance. A systematic error between the two independent measurement methods was found, but the uncertainties in the heat balance are higher due to the difficult evaluation of heat losses. Therefore, the results of the turbine flow meter are preferred and the linear regression coefficient amounts to 98.7%. For the further considerations in the analysis of the heat balance the heat losses were corrected by 2.1% to achieve consistency between the measurements of turbine and heat balance.

Figure 11.2.11 shows slices out of the time series from turbine and heat balance at a lead-bismuth temperature of 375°C and 100% pump power. In the left chart the deviation between the signals is lower than 1% and the limits of variation is ±0.02 m³/h which is in the range of the expected flow rate fluctuation in the THESYS loop.

After two weeks of correct continuous operation repeated collapse of the turbine flow meter signal was observed as shown in Figure 11.2.11 in the right graph. The assumption that a problem with the bearing of the rotor is responsible for the signal losses was confirmed a few days later by a post-failure
Figure 11.2.10. Flow rate measured by turbine and calculated from a heat balance as a function of pump power at lead-bismuth temperatures between 200 and 250°C in the THESYS loop of KALLA

![Graph showing flow rate vs. pump power](image)

Figure 11.2.11. Time series of flow rate acquired by turbine and heat balance before (a) and after (b) turbines bearing damage at 100% pump power at THESYS, KALLA

![Graphs showing flow rate over time](image)

analysis of the turbine: corrosion has destroyed the journal and bearing material at the heavily loaded spots, which were at the top of the bearing, because the rotor swam up in the heavy liquid metal. The turbine flow meter provides reliable data with a high accuracy, repeatability and linearity, but materials have to be found to assure a long term stability of the mechanical components in the liquid metal flow. Then a turbine flow meter could be used as a calibration device for PMF or EMFM systems.

11.2.2.2 Gyrostatic flow meters

The gyrostatic flow meter measures directly the mass flow in a tube. The measurement principle used is the coriolis force. If a liquid flows through a U-tube oscillating on axis A (see Figure 11.2.12), in both branches of the U-tube coriolis forces of opposite direction appear. They lead to an oscillation around axis B. The magnitude of the angle $\chi$ around axis B is directly proportional to the mass flow through the U-tube.
This measurement method is independent of the kinematic viscosity, the temperature, the flow profile and the gas content in the fluid. The used mass flow meter can dependent on the model be adjusted step-less in its measurement range via a remote control from the operation room. Moreover, the instruments offer the possibility to a self-calibration. For the calibration the fluid in the measurement tube has to be at rest. This can be done via two valves interconnected in the line at inlet and outlet of the mass flow meter. The accuracy of the mass flow meter is ±1% or 1/100 of the chosen scale.

The temperature operation range of the instrument is limited from -240°C to 204°C at a maximum pressure of 40 bars. But successful runs with sodium and sodium potassium alloys have shown its applicability to liquid metal systems, see e.g. [Barleon, et al., 1996] or [Stieglitz and Müller, 1996]. This temperature restriction is one of the most critical parts for the use in liquid metal systems. Also the component should not be installed close to magnetic fields due to the electronics in the instrument in order to avoid disturbances in the electronics.

11.2.3 Pressure- and counter-based flow meters

11.2.3.1 Von Kármán vortex street flow meter

If a fluid flow passes a cylindrically shaped body a Kármán vortex street is formed downstream which is characterised by a periodic vortex arrangement of counter rotating vortices as depicted in Figure 11.2.13. The frequency of the periodically detaching vortices is directly proportional to the fluid velocity \( u_m \) within a certain velocity threshold. The frequency of the vortices \( f \) in liquid metal flow can be detected, e.g. by a simple pressure transducer or any other mechanical device. The two dimensionless physical numbers describing this simple problem are the Strouhal number \( Str \) and the hydraulic Reynolds number \( Re \) built with the diameter \( d \) of the cylinder.

\[
Str = \frac{f d}{v_0} \quad \text{and} \quad Re = \frac{u_m d}{v} \quad (11.10)
\]

The Kármán vortex street is a regular hydrodynamic instability existing in a Reynolds number regime between \( 60 \leq Re \leq 5 \times 10^3 \). Beyond this Reynolds number range a full turbulent mixing appears and the regular structure of the vortices too. Nevertheless, taking use of the vortex pattern formation and the simple count of fluctuations (the absolute magnitude of the signal does not matter) the v. Kármán vortex street flow meter represents a simple tool to measure extremely small velocities. For Reynolds numbers \( Re \geq 60 \) the Strouhal number of a flow around a cylinder is constant at a value of \( Str = 0.2 \). Considering a lead bismuth temperature of \( T = 300^\circ \text{C} \) and a cylindrical rod with a diameter of \( d = 6 \text{ mm} \) the smallest resolvable velocity is 1.7 mm/s. The frequency to be counted by a pressure gauge is then \( f = 0.06 \text{ Hz} \).
Of course, using this measurement technology some constraints regarding the inlet conditions exist. The flow facing the cylindrical obstacle has to be fully developed in the sense that no lateral pressure gradients appear and the axial derivatives in flow direction are zero. This leads for turbulent flows immediately to developing length of at least 30 hydraulic diameters of the pipe. A technical feasible solution to overcome this long developing length, which is in case of a 60 mm tube about 1.8 m, is the installation of a flow straightener, which equalises the flow. Depending on the installation environment an arrangement of parallel small tubes may be not sufficient, for instance directly after a 90° bend.

However, due to the small kinematic viscosity of lead bismuth a Reynolds number of \( Re = 5 \times 10^3 \) is very fast exceeded. In the intermittent Reynolds number regime \( 5 \times 10^3 \leq Re \leq 2 \times 10^4 \) the Strouhal number is not constant and thus not directly related to the mean velocity in the duct. In this specific regime the v. Kármán technique can be used only with additional calibration procedures, e.g. against a PMF or an EMFM. For \( Re \geq 2 \times 10^3 \) the Strouhal number again shows an almost constant proportionality with the frequency. But it has to be stated that at high Reynolds numbers a non-linear correction has to be applied, which depends on the obstacle inserted in the duct. A calibration of the flow meter in the loop is hence inevitable.

### 11.2.3.2 Obstacle flow meters, nozzle and orifice flow meters

A combination of the v. Kármán flow meter with a pressure difference measurement method, as depicted in Figure 11.2.14, turned out to be a technically feasible solution. The pressure difference measurement method takes advantage of the fact that the pressure loss \( \Delta p \) of the flow around a circular obstacle expressed in terms of a \( c_W \) value is at Reynolds numbers of \( Re \geq 5 \times 10^3 \) independent of the Reynolds number. The mean velocity \( u_m \) in the duct and hence the flow rate can be calculated using Eq. (2.11):

\[
    u_m = \frac{2 \Delta p}{\rho c_W}
\]

(11.11)

The \( c_W \) values may be taken from [Beitz and Küttner, 1986] or other standard handbooks. In case of a 60 mm tube and a cylindrical rod with a diameter of 6mm the \( c_W \) value is \( c_W = 0.82 \). The independence of the \( c_W \) values of the Reynolds number holds up to \( Re \sim 5 \times 10^7 \). In order to measure small velocities and to calibrate both techniques against each other pressure transducers resolving smallest pressure differences are required.
Operational characteristics

Here, in the THESYS loop we used pressure transducers capable resolving an absolute pressure of 12.5 Pascal. Thus, the minimal velocity to be resolved by the pressure difference method is a mean velocity of $u_m = 0.05$ m/s. To summarise, in case of the THESYS loop the operational range of the Kármán vortex street flow meter is from $1.7 \times 10^{-3} \leq u_m \leq 0.146$ (m/s) and the corresponding range of the pressure difference method is from $5 \times 10^{-2} \leq u_m \leq 14.6$ (m/s), which is far beyond the technical capabilities of the THESYS loop. In Figure 11.2.15 the technical set-up of the combined flow meter type being installed in THESYS is illustrated.

Figure 11.2.15. Combined pressure difference and Kármán vortex flow meter as it is used in THESYS and THEADES. (b) Flow straightener being installed upstream the flow meter. (c) Flange for insertion of cylinder and pressure taps.

Orifices, nozzles or Venturi nozzles as illustrated in Figure 11.2.16(a) are commonly used flow meters and a broad overview is given in the [DIN tables, 1982]. The pressure loss coefficients $\xi_2$ related to the smallest cross-section $d_2$ are shown in Figure 11.2.16(b) as a function of different diameter ratios $d_2/d_1$. The data have been collected from [Herning, 1966] and [White, 1986]. Using the continuity condition the pressure drop coefficient $\xi_1$ is obtained from Eq. (11.12).

$$\xi_1 = \left( \frac{d_1}{d_2} \right)^2 \cdot \xi_2$$
Knowing $\xi_1$ the mean velocity $u_m$ and hence the flow rate can be calculated using Eq. (11.13):

$$u_m = \sqrt{\frac{2\Delta p}{\rho\xi_1}}$$  \hspace{1cm} (11.13)

where the pressure difference $\Delta p$ is measured between the positions indicated in Figure 11.2.16(a).

Figure 11.2.16. (a) Orifice designs used for flow rate measurements. (b) Pressure drop coefficient $\xi_2$ as a function of the diameter ratio $d_2/d_1$ for the different orifice geometries from figure (a)

Pitot and Prandtl tubes also often used to measure flow rates rely also on the measurement of pressures. By means of positioning the tube as depicted in Figures 11.2.17(a), (b) in the flow the total pressure $p_0$ can be measured by:

$$p_0 = p_1 + \rho_{\text{meas}} gh,$$  \hspace{1cm} (11.14)

where $p_0$ is the absolute outer pressure and $\rho_{\text{meas}}$ the density of the measurement fluid. Using Pitot tubes an absolute pressure transducer is connected at the end of the line so that $p_1$ is given for $u = 0$. The dynamic pressure $p_{\text{dyn}}$ can be calculated from the difference of the total pressure $p_0$ and the static pressure $p_{\text{stat}}$ using a Prandtl tube.

By measuring $p_{\text{dyn}} = p_0 - p_{\text{stat}} = \rho_{\text{meas}} gh$ the local velocity $u(z)$ can be calculated using Eq. (11.15):

$$u(z) = \sqrt{\frac{2 p_{\text{dyn}}}{\rho}}$$  \hspace{1cm} (11.15)
While using Pitot-tubes as flow rate measurement devices, at least two-sensors have to be located within the tube according to ISO3966-1977, see Figure 11.2.17(d). Since the velocity profile varies as a function of dimensionless radius \( r/D \) the Pitot tubes have to be placed in such positions where this deviation is minimal. In Figure 11.2.17(c) the dimensionless velocity is depicted as a function of the radius [VDI, 2001]. It shows that at \( r/D = 0.381 \) in a Reynolds number range \( Re = 4 \times 10^3 - 3.2 \times 10^6 \) the deviation is less than 3%. Another error source while using Pitot tube flow meters is that they require a developing length of at least 25 tube diameters after a \( 90^\circ \) bend. For developing lengths of more than 35 diameters the systematic error is minimised to less than ±0.5%.

Figure 11.2.17. Local flow velocity measurements using Pitot (a) and Prandtl tubes (b). (c) Local axial velocity normalised by the mean velocity as a function of the dimensionless radius \( r/D \) at different Reynolds numbers \( Re \). (d) Schematic set-up of the Pitot flow meter.

11.2.4 Ultrasound transit time method (UTT)

The velocity of propagation of sound waves in moving fluids changes with the flow velocity of the transmitting medium. An ultrasound wave is sent through a fluid under an angle \( \alpha \) to the flow direction from a sender A to a receiver B as shown in Figure 11.2.18 [Gaetke, 1991] and [Millner, 1987].

If the fluid is not moving the signal travels with the sound speed \( c \) from A to B from what the transit time is calculated to \( t_0 = L/c \). But if the fluid flows with the mean velocity \( u_m \) the signal is accelerated by the portion of the projection of this velocity to the measurement line. Accordingly the
signal is decelerated by the same amount on its way from B to A. The transit times of the signals can then be calculated by:

\[ t_{AB} = \frac{L}{c + u_m \cos \alpha} \quad \text{and} \quad t_{BA} = \frac{L}{c - u_m \cos \alpha} \tag{11.16} \]

Transformation yields to an expression for the mean flow velocity:

\[ u_m = \frac{L}{2 \cos \alpha} \left( \frac{1}{t_{AB}} - \frac{1}{t_{BA}} \right) \tag{11.17} \]

In practice the determination of the transit time difference from the phase shift between the two signals \( \Delta t = t_{AB} - t_{BA} \) is common and with the postulate \((u_m/c)^2 \ll 1\) one obtains:

\[ u_m = \frac{c^2}{2L \cos \alpha} \Delta t \tag{11.18} \]

Compared to Eq. (11.17) in expression (11.18) the mean velocity depends on the sound speed. This disadvantage is accepted because the determination of the usually very short transit times appearing in Eq. (11.16) is technically difficult and less accurate than the identification of its difference. Due to the fact that beside the sound speed only geometric measures occur in the equation, the ultrasound transit time method can be used for calibration of other measurement methods if the sound speed in the fluid is known and a fully developed flow profile is present.

**Figure 11.2.18. Principle of ultrasound transit time measurement** freely adapted from [Gaetke, 1991]

To generate ultrasound mainly piezoelectric materials are used (quartz, lead zirconate, barium titanate) whose Curie-temperature, above which they get instable and irreversible destroyed, limits the applicable temperature range to a maximum of about 150°C. For measurements in high temperature fluids like liquid metals wave guides are required. [Liu, et al., 1998] have developed bundled wave guides at the company Panametrics for ultrasound transit time measurements in fluids and gases for
temperatures up to 450°C. They describe wetted and clamp-on systems and show results of their application for flow rate measurements at temperatures between 200 and 300°C. The fact that ultrasound is transported as a longitudinal pressure fluctuation also in opaque media turns it into a promising method for measurements in liquid metals.

In order to transport a significant energy through the structure into the fluid the material thickness of the emitter has to be adapted to the fluid. Here, the impedance $Z$ which is the product of the sound speed $c$ and the density $\rho$ has to be taken into account. The permittance $D$ of an acoustic wave through a solid-fluid interface can be expressed as a function of the thickness of the material $d$, the wavelength $\lambda$ of the sound wave and the impedance of the fluid and the liquid $Z_i$ according to Eq. (11.19):

$$D = \frac{1}{\sqrt{1 + \frac{1}{4} \left( \frac{m-1}{m} \right)^2 \sin^2 \frac{2\pi d}{\lambda}}}$$

(11.19)

The permittance of a steel plate for a longitudinal wave at a frequency of 4MHz towards water and lead-bismuth as a function of the thickness is shown in Figure 11.2.19. This permittance is only achieved if the interface is perfectly physically wetted in the adhesive sense and no mode transitions of the wave at the interface appear.

Figure 11.2.19. Permittance $D$ of steel at a frequency of 4 MHz as a function of the plate thickness $d$ for the interface steel-water and steel-PbBi

Other sources of uncertainties using the ultrasound are the absorption and the sound scattering. Finally, the anisotropy of the sound speed has to be taken into account. In case of measuring flows containing a temperature gradient, the sound speed varies with the square root of the temperature and thus the temperature has to be known and adequate countermeasures to be foreseen.

The mode transition problem at the interface leading to a significant decrease of the signal magnitude is solved by a specific sensor design. The mode transitions can in principle occur due to:

a) longitudinal to transverse wave transitions;

b) surface waves like Rayleigh-waves;

c) creep waves;

d) ring sound.
Operational characteristics

Crucial for the coupling of ultrasound is an adhesive wetting of the wave guides ends to transmit the oscillation energy into and out of the fluid. Hence, to guarantee the wetting a 2 μm thick sacrificial nickel layer can be applied on the wave-guides in a galvanic bath. Due to the high solubility of nickel in lead-bismuth the wetting can be preserved for the duration of the application, which results in 60% of the senders signal amplitude at the receiver.

Figure 11.2.20 shows the flow rate over pump power measured by means of the USTT and the PMF methods at two temperature levels. The PMF was calibrated at 70% pump power like described above and shows a good agreement with the USTT values at the other settings. The flow rates measured at a temperature of 376.5°C are about 5% higher than the ones at a temperature of 208.4°C, which is caused by a slightly better performance of the EM-pump at higher temperatures due to a lower contact resistance between the liquid metal and the pump channel.

Figure 11.2.20. Flow rate measured by USTT and PMF at temperatures of 208.4°C and 376.5°C as a function of the pump power

The nickel coating of the wave guides results in a stable coupling and therefore a small uncertainty of lower than 1% for flow rates of more than 0.5 m³/h. The linear regression coefficient is calculated from the measurements at 376.5°C to 99.8%. Systematic errors occur in consequence of the test sections thermal elongation, which changes the length of the sound path appearing in Eq. (11.18). This error can be calculated to ~3% so that the complete uncertainty sums up to ~4%. For the Panametrics XMT868 a measuring range of ±12.2 m/s at an uncertainty of ±2.5% of the reading is given and coincides with the ascertained value. In principle bigger pipe diameters and higher flow rates reducing the errors and improving signal to noise ratio for the USTT method, because the transit time differences increase. In addition multiple ultrasound paths circumferentially arranged around the pipe can also increase the accuracy.

11.3 Pressure sensors

11.3.1 Types of pressure gauges and operation experience

Generally two types of pressure measurement devices are available in more or less direct contact with lead-bismuth. These types of sensors are also capable to measure local velocity distributions if
they are used in the context of a Pitot or Prandtl tube. Additionally, they can be used as flow meters of different principles in case an elevated pressure drop in the piping can be accepted by the individual user.

The first are the capacitive transducers illustrated in Figure 11.3.1, which measure the pressure difference ($\Delta p$) between two discrete points in a piping system. The pressure signal is absolutely obtained by an electric capacity change between to plates, here filled with silicon oil. As the transducer medium is only capable to withstand temperatures less than 250°C the connection between the liquid PbBi and the transducer itself is realised by an incompressible coupling medium. Here, often the eutectic sodium-potassium alloy Na$_{78}$K$_{22}$ is used with a melting point of -11°C. The use of a coupling medium limits the temporal resolution. The frequency response time of the transducer is typically limited to 5 Hz, which does not allow to measure fast fluctuations like velocity or flow rate oscillations. Figure 11.3.1(a) depicts a technical sketch of the difference pressure measurement sensor used in the Karlsruhe Lead Laboratory (KALLA). Nevertheless, the major advantage of the capacitive methods is their excellent stability and accuracy. They offer a high resolution ($\pm 12.5$ Pascal), an absolute pressure signal, which is attractive for reactor applications, and additionally the zero point can be easily determined. But, they require a complex set-up of heating elements in the transmission line up to the coupling clutch, a precise fill and drain strategy to avoid bubbles and they are actually expensive.

**Figure 11.3.1.** (a) Schematical set-up of a capacitive pressure difference transducer using a coupling medium. (b) photograph of an absolute pressure transducer using a fast Wheatstone bridge. (c) Test stand to measure liquid levels and pressure differences erected at ENEA/Brasimone.

Another method to measure absolute pressures $p$ is to use pressure gauges based on a fast Wheatstone bridge. These kinds of sensors are compact and can be directly screwed in any tap of the liquid containing piping. Due to their small dimension they have a negligible inertia and hence allow to detect fast oscillations of order of several hundred Hz. A photograph of such a sensor is shown in Figure 11.3.1(b). Due to the fabrication principle the maximal span is given and a calibration before each experimental run must be performed. Then, the pressure resolution is similar to that of the capacitive units. Nevertheless, this techniques which can sustain up to 480°C liquid metal temperature, is the preferred option for use in the Pitot and Prandtl tubes later described and used for recording local velocities.
A third option to measure pressures, differential pressures, liquid levels or flow rates is the bubbling technique, successfully performed in the lead bismuth loop CIRCE of ENEA. Here, bubbles of inert gas are injected via Venturi tubes into the liquid. While measuring the gas pressure in the bubble tubes, levels and pressures can be recorded at several locations simultaneously using only one sensor, which is not in direct contact with the liquid and thus temperature limitations for the use of such a kind does not exist. The technical realisation of a test stand proving this principle at ENEA is illustrated in Figure 11.3.1(c). Besides simple set-up of the pressure cells operating at room temperature and the simultaneous recording at several positions the low price is rather attractive. Nevertheless, all results depend on the nozzle shape, the detailed positioning in the system and moreover an extensive calibration. Further, the temporal resolution is rather limited and a temperature correction must be performed because the surface tension of the liquid depends on it.

11.3.2 Pressure correction in fully developed turbulent pipe flow

Especially, in very fine resolution measurements, say, e.g. in benchmark experiments it may appear that misreadings of the wall static pressure occur, which are related due to the finite size of the pressure tapping. This effect was observed over a wide range of Reynolds numbers by numerous authors long ago as shown in the papers by [Allen & Hooper, 1932], [Ray, 1956], [Thom & Appelt, 1957], [Rayle, 1959], [Livesey, et al., 1962] but also by [Franklin & Wallace, 1970] and [Ducruet & Dyment, 1984]. A summary of the complete literature dealing with this problem is given by [Chue, 1975].

All results indicate that the correction term as a fraction of the wall stress continues to increase as the hole Reynolds number $d' = (u_d)/\nu$ increases. For small holes relative to the pipe diameter the results follow a single curve, but for larger holes the data diverge from this universal behaviour at a point that depends on the ratio of the holes diameter to the pipe diameter. This effect becomes pronounced especially for large Reynolds numbers, which appear easily in heavy liquid metals because of their low kinematic viscosity $\nu$. A flow structure within a pressure tapping yielding the pressure error is schematically shown in Figure 11.3.2.

Figure 11.3.2. a) Flow structure within the static pressure tapping.
b) Variation of the non-dimensional pressure error $\Pi$ as a function of the holes Reynolds number $d'$ for different $d/D$ after McKeon & Smits (2002).

A dimensionless analysis performed by [McKeon and Smits, 2002] shows that the pressure error $\Delta p$ depends on the hole diameter $d$, the hole depth $l$, the diameter of the connection to the transducer $d_c$, the wall shear stress $\tau_w$, the fluid density $\rho$ and the kinematic viscosity $\nu$. Within this context the
characteristic length scale of the facility, where the experiment is conducted, namely the pipe diameter $D$ is important especially considering large holes. Then the non-dimensional error $\Pi$ can be expressed by a dimensionless parameter group in the form:

$$\Pi = \frac{\Delta p}{\tau_w} = f\left(\frac{d u_r}{v}, \frac{d}{D}, \frac{l}{d}, \frac{d_r}{d}\right)$$

with $u_r = \sqrt{\frac{\tau_w}{\rho}}$

(11.20)

where $u_r$ is the friction velocity. Assume first that $d/D$, $ld$ and $d/d$ are constant then the pressure error $\Pi$ depends only on $d^+$. With decreasing hole Reynolds number $d^+$ (namely $d\to0$) $\Delta p$ tends to zero. Far from the wall dynamic and turbulent effects dominate the flow behaviour and thus for large $d$ the ratio $d/D$ becomes important. Shaw (1960) investigated the hole Reynolds number $d^+$ effect in a 50 mm diameter tube for flow Reynolds number up to $Re = 1.7 \times 10^5$. He found that the non-dimensional error $\Pi$ increases with increasing $d^+$ but reaches an asymptotic limit of 3 for $d^+ = 750$. But he dismissed the effect $d/D$, because as $d$ increases not only the hole Reynolds number increases but also $d/D$. Shaw suggested that the hole must become large enough to change the flow field itself and postulated this occurrence to appear at $d/D \sim 0.1$. For $d/D > 0.1$ the global flow pattern in the pipe and which is even more important the flow over the tapping is changed leading to a miscellaneous pressure reading. In this case a correction due to the secondary flows appearing the pressure tap has to be performed. Further literature treating this topic may be taken from [Pozrikidis, 1994], [McKeon & Smits, 2002] or [Ligrani, et al., 2001].

The depth to diameter plays also a role in the pressure error, since it dictates the eddy system set-up within the cavity. Even the Allen & Hooper investigations 1932 show, that the error increases with $ld$, but if $ld$ exceeds the value 2 [Chue, 1975] showed by a compilation of all previous experiments an asymptotic value is reached, which represents the “deep” limit for all Reynolds numbers. Consequently, a wide cavity behind the tapping reduces the error, while a contraction in diameter from the tapping to the pressure gauge can increase the error, see e.g. [Livesey, et al., 1962].

As a practical guide, it is suggested that if a Pitot tube and static tapping are used to make pressure measurements within a pipe flow, the static tapping should have a large and constant $ld$, at least $ld > 2$ to ensure that the flow structure within the cavity is fully developed and not changing with the Reynolds number. Second, a small ratio of tapping to pipe diameter has to be set-up, to prevent the tapping fundamentally altering the external flow.

11.4 Local velocity measurements

The viability of technical units like beam windows or fuel bundles requires often sophisticated information on the local velocity distribution and local heat fluxes in the geometry, which often can not be simulated numerically. The opaqueness of liquid metals excludes the use of optical methods which are commonly used in thermal-hydraulics. The intention to develop new measurement techniques to determine the local velocities in liquid metals arises from the following requirements:

a) Although there is a growing interest in measuring the local velocities in opaque fluids at high temperatures most of the currently developed techniques are only existent on laboratory scale and show no reasonable accuracy over a sufficiently long time period.

b) The measuring conditions in liquid metal facilities are often characterised by external magnetic fields or strong electric noise caused by heating elements, pumps or high power supplies.
c) Disturbances of the flow caused by the presence of the sensor should be prevented as much as possible.

d) The measurement range should cover low (mm/s) as well as high values of the velocity in terms of several meters per second.

This chapter presents a few measurement principles applied in the past decades successfully to liquid metal flows. Moreover, the operation principle, the necessary calibration methods and correction factors are described or the appropriate literature sources are cited.

For the intrusive methods like e.g. reaction probes, fibre mechanical probes, permanent magnetic probes or Pitot tubes corrections are necessary accounting for the impact of the probe on the velocity field to be measured experimentally. This effect is discussed extensively in the chapter of the Pitot tube, but it can be generally applied to all other intrusive methods.

11.4.1 Ultrasound Doppler velocimetry

A non-intrusive method to measure instantaneously whole velocity profiles is offered by the ultrasound Doppler velocimetry (UDV). The UDV technique is based on sending ultrasound pulses through the liquid instead of a continuous wave. The echoes from particles immersed in the fluid (which requires a flow seeding) are sampled. The related velocity information is obtained from the shift in position of scatters between ultrasound pulses and not from the Doppler frequency shift of the echoes. Hence, the velocity information is yielded from a correlation function. One of the major advantages of UDV is that it is a non-intrusive method, with which the velocity is scanned not only at one exclusive position like in a laser Doppler anemometer. It rather samples velocity information instantaneously at several positions along the ultrasound wave path. The operation principle is shortly explained and sketched in Figure 11.4.1.

The location of the measurement volume is given by relation (11.21)a, in which \( c \) is the sound speed and \( t_d \) the actual travelling time of the pulse. The spatial shift of the position \( \Delta P \) between two pulses applying a pulse repetition time \( t_{prf} \) is given by Eq. (11.21)b.

\[
P = \frac{c t_d}{2} \quad \text{and} \quad \Delta P = (P_2 - P_1) = u(z) t_{prf} \cos \theta = \frac{c \left( t_2 - t_1 \right)}{2}
\]  

(11.21)  
a,b

The time difference \((t_2 - t_1)\) is recorded by means of the phase shift of the echoed signals and can be expressed by relation (11.22)a, where \( f_e \) is the echo velocity. Finally, the velocity \( u(z) \) at a discrete co-ordinate \( z \) can be evaluated by Eq. (11.22)b.

\[
\Delta d = 2\pi f_e (t_2 - t_1) \quad \text{and} \quad u(z) = \frac{c \Delta d}{2 f_e \cos \theta t_{prf}} = \frac{c f_d}{2 f_e \cos \theta}
\]  

(11.22)  
a,b

with \( f_d \) representing the Doppler shift. Of course, an upper limit of the maximum measurable velocity and the maximum measurement depth exists. This constraint is expressed by the relations (11.23).

\[
u_{\text{max}} = \frac{c}{4t_{prf} f_e \cos \theta} \quad ; \quad y_{\text{max}} = \frac{c t_{prf}}{2}
\]  

(11.23)  
a,b
The UDV technique allows the instantaneous acquisition of whole velocity profiles. This is performed by a reconstruction of the velocity information in the following way. First, the length of the acquired echoes reflected from the particles within the fluid is divided into intervals of the temporal length $\Delta \tau_i$. The run time $\tau_i$ is associated with a measurement position in the duct $y_i$ via the relation:

$$y_i = \frac{c\tau_i}{2} \quad (11.24)$$

Then the velocity within a discrete interval $u_i$ can be calculated. This procedure determines the local resolution and the size of the measurement volume, which is given by the relations (11.25).

$$\Delta y_i = \frac{c\Delta \tau_i}{2} \quad \text{and} \quad \Delta y_e = \frac{c\Delta \tau_e}{2} \quad (11.25)$$

The whole process of the acquisition of a velocity profile is sketched in Figure 11.4.1.

**Figure 11.4.1. Operation principle of the ultrasound Doppler velocimetry (UDV) to acquire local velocities in heavy liquid metal flows from Lefhalm (2004)**
Another feature of the UDV technique is that it allows to measure even deep into the boundary layer close to the duct wall and thus is able to measure velocities only a few microns away from the wall. For this purpose wall correction functions have to be applied, which account for the fact that a part of the measurement volume is located within the wall. In order to get the correct velocity contribution from the fluid domain only echoes from the fluid region are sensed. In a next step the mass centre of the fluid/wall interval is calculated. The deviation of the mass centre of the fluid/wall interval from the distance centre yields a displacement of acquisition point. A detailed description of this procedure may be taken from [Wunderlich, et al., 2000], [Nowak, 2002] or [Lefhalm, 2004].

The measurements of the velocity profiles within the turbulent boundary layer of an annular duct performed by [Lefhalm, 2004], which are shown in Figure 11.4.2(a) illustrate that by means of correction functions the velocity can be acquired. The measured velocities coincide with the literature data of [Reichhardt, 1951] almost perfectly. The deviations found are less than 5%. Moreover, it was possible to measure into the viscous sublayer up to values of \( y^+ \approx 3 \). In his experimental configuration this corresponded to a wall distance of 46 \( \mu \text{m} \). Also the measurement of the turbulent fluctuations within the boundary layer are possible using the wall correction procedure. Only for \( y^+ < 10 \) the RMS resolution rapidly dropped.

**Figure 11.4.2.** a) Measured turbulent velocity profiles in the boundary layer in an annular duct of \( \Omega = 60 \text{ mm} \) at \( Re = 8.1.10^4 \) and comparison with [Reichardt, 1951]. b) Comparison of the velocity fluctuations (RMS) with [Durst, et al., 1996].

From the procedure explained above it is clear that numerous effects contribute to the acquisition of a proper signal and in fact about 100 parameters are necessary to define the measurement process. The enormous sound speed of heavy liquid metals like PbBi requires extremely fast acquisition and data processing systems to obtain reliable velocity information. Besides these quite sophisticated demands on the data transmission recording and processing units [which are depicted in Figure 11.4.3(d)] several constraints regarding the environmental conditions have to be fulfilled. One of the most crucial problems is the elevated temperature of more than 200\(^\circ\)C in typical liquid metal applications, which can not be sustained by commercially available Bariumtitanat sensors (BaTiO\(_3\)). Thus, wave guides have been developed to decouple the temperature from the sensor. Such an integrated probe consisting of a wave guide and a sensor is shown in photograph 11.4.5(b). It was initially developed by the Forschungszentrum Rossendorf and is in principle applicable to liquid metal temperatures up to 620\(^\circ\)C, see [Eckert, et al., 2003]. Secondly, an acoustic coupling of the sensor and the fluid has to be ensured, which in principle means that the probe has to be physically wetted. This is partially achieved by applying a sacrificial nickel layer on the probe surface before inserting it through the fluid. Within the lead-bismuth this nickel layer is dissolved and ensures for a certain time the wetting of the surface. However, after a few days of operation the wetting of the sensor surface gets lost.
The study of the wetting behaviour of lead bismuth on steel surfaces is a task which as to be solved not only for this application. Another problem is the long term stability of the probe and the flow seeding. By means of conditioning the oxygen content within fluid a certain long term stability of the probe was achieved and a sampling of velocity profiles was successfully performed without any additional artificial flow seeding. Artificial flow seedings with particles of a density like the lead-bismuth are hardly available and stable within the operational conditions typically used.

Nevertheless, it is a question to be clarified in the current programme whether lead bismuth clusters or other impurities are responsible for the generation of the echoes. If temperature gradients are present in the flow being studied, travelling time corrections have to be applied, because the sound speed depends on the square root of the temperature. Thus, either the temperature field of the studied flow has to be known or temperature correlations have to be used. Besides the numerous difficulties using UDV within the THESYS loop KALLA velocity measurements have been successfully performed in a turbulent PbBi pipe flow at temperatures up to 400°C. In Figure 11.4.3(e) the measured mean velocities are shown as a function of the pipe depth for different pump power levels (here given in %). Within this campaign velocity fluctuations of frequencies up to 15 Hz were recorded. If appropriate wall correction functions are used even the velocity distribution in wall near boundary layers can be detected as shown in [Lefhalm, 2004].

### 11.4.2 Permanent magnetic probes (PMP)

Another method to measure fluid velocity within an electrically conducting fluid is given by permanent magnetic probes. The permanent magnetic probe (PMP) contains a miniaturised permanent
magnet located perpendicular to the main flow. The magnet is encapsulated within a steel tube. The PMP probe allows to measure simultaneously the velocity and the temperature similar like the combined Pitot tube presented in § 11.4.1. The turbulent heat fluxes can be determined from the cross-correlation of both signals – temperature and velocity fluctuations.

**Figure 11.4.4.** (a) Photograph of a miniaturised PMP probe with thermocouples from Kapulla (2000). b) Side and top view of the arrangement of the thermocouples within a PMP probe.

The PMP probe signal is obtained as low ohmic electric potential $\Delta\phi$ arising from the interaction of the flow field $u$ with the magnetic field $B$. The simplified Ohms law for moving electric conductors and temporal steady magnetic fields reads to:

$$
\mathbf{j} = \sigma (E_e + E_{th} + u \times B)
$$

(11.26)

where $j$ is the current density, $\sigma$ the specific electric conductivity of the fluid, $E_e$ the electrostatic field, $E_{th}$ the thermo-electric field, $u$ the integrated velocity of the probe dimension and $B$ the magnetic induction. Generally, there are two main disturbances affecting the induced electric potential. If one takes into account the Maxwell equations [Eqs. (11.27)a-c] and the simplified Ohms law [Eq. (11.26)] one obtains Eq. (11.28).

$$
\nabla \times B = \mu \mathbf{j}; \quad \nabla \times E = 0; \quad E = -\nabla \phi; \quad \nabla \cdot B = 0
$$

(11.27)

where $\mu$ is the magnetic permeability given by $4\pi 10^{-7}$ As/Vm.

$$
E_{th} = -S \nabla T - Q (\nabla T \times B)
$$

(11.28)

in which $S$ is the thermoelectric coefficient in V/°K and $Q$ the Nernst-Ettinghausen coefficient in V/(°K Tesla). Thus, in order to calibrate the probe isothermal measurements are required in a flow with a defined velocity field. A detailed description of this procedure may be taken from [Ricou & Wives, 1982], [Weissenfluh, 1986] and [Kapulla, 2000]. The calibration yields the specific Seebeck coefficient of the individual probe. Additional care has to be taken if external magnetic fields are present in the domain of interest as, e.g. near to electromagnetic pumps or close to DC electromagnetic flow meters. Then an even more complicated effort has to be spent in order to determine the coefficients of the probe. The methodology necessary in this case is exhaustively elaborated in the work of [Ricou & Wives, 1982] and more precise in [Müller, et al., 2005].
In the absence of external magnetic fields the PMP probe allows to detect liquid metal velocities in the range from 0-10m/s with an extreme high sensitivity of about 1 mm/s as the experimental works of [Horanyi & Krebs, 1988], [Knebel & Krebs, 1994], [Ricou & Vives, 1982] and [Weissenfluh & Sigg, 1988] document. The sensitivity and the velocity range is not restricted and scopes several decades, which is not possible with other techniques. Generally this technique is applicable up to temperatures of 720°C as the paper by [Ricou & Vives, 1982] shows with measurements in mercury, aluminium, tin, zinc and some alkali metals. The upper limit of the temperature is given by the Curie temperature of the magnet, which is e.g. for nickel-based permanent magnets about 860°C, see e.g. [Eringen, 1980]. Due to responses that are steady, instantaneous and proportional to the velocity of the liquid metal flow high temporal resolutions can be resolved, which is necessary for the study of turbulent flows.

Although it is an intrusive method modern fabrication technologies allows to miniaturise the PMP probe down to diameters less than 2 to 3 millimetres and thus to minimise the impact of the probe on the flow.

One of the most crucial problems of the PMP is the wetting behaviour in the sense of an electrochemical wetting without any contact resistance between the fluid and the probe. Regarding the alkali metals this is not a problem. However, lead and its alloys show a poor electrochemical wetting behaviour of steel surfaces. Similarly as for the UDV probe the PMP has been plated with nickel or silver as a sacrificial layer, which is dissolved immediately by the lead bismuth in order to ensure a proper wetting of the sensor. Nevertheless, after two weeks exposure of the probe to lead bismuth in the composition Pb45Bi55 at 400°C the wetting got lost even in an oxygen controlled atmosphere. Also within a reducing atmosphere by means of hydrogen input into the loop the wetting of the probe could not be recovered again, see [Knebel, et al., 2003]. This wetting problem is an issue which is not fully understood currently and requires a detailed investigation in order to develop HLM adapted sensors.

### 11.4.3 Reaction probes (RP)

Especially in steel and aluminium casting or in molten salts where the liquid is highly corrosive reaction probes are used, which are based on the measuring of the force exerted on a submerged body by the flowing liquid. The submerged bodies used in different studies could be discs, plates or spheres. The operation principle of a reaction probe sensor is akin that of a Pitot tube, in that the device responds to the stagnation pressure developed when the fluid impacts the disc. The flow velocity \( u \) can be easily calculated using Bernoulli’s equation:

\[
    u = \sqrt{\frac{2F}{A}}
\]

where \( F \) is the force on the disc and \( A \) its area. A sketch of such a reaction probe is shown in Figure 11.4.6(a). Here the flow faces the disc and the connected wire compresses a spring. By measuring the compression using a triangulation method the mean velocity can be calculated. The fluctuations are captured by a strain gauge. Even in this simple set-up the measurements of [Szekely, et al., 1977] showed quite sensible and reproducible results. Especially the temporal resolution of the probe was quite fine. Also the disc probe requires a specific calibration procedure and it can be only used in a limited velocity range, due to the secondary flow, which is induced by the disc. Moreover, this simple sensor is only capable to detect one velocity component. But, due to the decoupling of the sensor element from the liquid with its elevated temperatures conventional and reliable technology can be used.
A more sophisticated design of a reaction probe was developed by [Moore & Hunt, 1982], in which the drag force acting on a sphere is utilized to deduce the velocity. This probe type is depicted in Figure 11.4.6(b). They used a perforated sphere in order to eliminate the vortex shedding effectively and to increase the drag. In their set-up the sphere was made of tantalum with a diameter of 5 mm. Strain gauges are bonded to either sides of the steel strip which is connected via a 1 mm wire to the sphere.

The signals from the drag reaction probe can measure the drag experienced by the shell and the connecting wire. The mean drag force $D$ integrated over the sphere facing the flow is related to the velocity by:

$$D = \frac{1}{2} \rho A' C_D u^2$$  \hspace{1cm} (11.30)

where $\rho$ is the specific density, $A'$ the cross-sectional area normal to the flow and $C_D$ the drag coefficient, which depends in most cases on the Reynolds number. According to [Schlichting, 1979] the drag coefficient of a sphere, however, is in the Reynolds number range from $2 \times 10^3 < Re < 2 \times 10^5$ almost constant. In the study performed by Moore & Hunt (1982) this was accomplished by the proper selection of the dimensions of the tantalum sphere. After a calibration in a annular duct flow the probe showed an excellent performance regarding the mean velocity fields, see [El-Kadah & Szekeli, 1984]. Because of the high temporal resolution of the strain gauges a large bandwidth of oscillations of the turbulent flow could be captured so that fast Fourier transforms up to 2-3 kHz could be performed. A comparison of the duct flow data with numerical studies computed by [Evans & Lympany, 1983] demonstrated that the precision achieved with this type of reaction probe was the best compared to similar probe type and matched the model better than 5%.

The initial probe designed by Moore& Hunt was modified by [Moros, et al., 1985] in such a way as to measure simultaneously the vertical and one of the horizontal velocity components. A sketch of the [Moros, et al., 1985] reaction probe type is shown in Figure 11.4.7.

As all reaction probe types are intrusive methods, their numerous shortcomings include:

a) **Mechanical oscillations.** The oscillation of the suspended probe has to be kept within an acceptable range so as to resolve the desired velocity value. The sensor must be mechanically decoupled from the piping to avoid miscellaneous readings. The design of the drag element and the connection wire predetermines the damping of the sensors and thus its temporal resolution.

b) **The dimension of the drag body.** The dimension of drag body and wire must be chosen in such a way to keep the drag coefficient in the velocity range of interest most insensitive to the
Reynolds number. Otherwise a time consuming calibration over the whole velocity range to be expected in the individual geometrical experimental set-up must be performed in a reference experiment to measure $C_D(Re)$.

c) Impact of the probe on the flow. Since the body of the reaction probe induces secondary flows it impacts and modifies the flow to be measured. The pressure waves may have an upstream effect and the secondary flows induced by the drag body may change the flow in such a way that the effect to be measured can be hidden behind the artificial flow modifications. Thus, the flow field in the experimental set-up to be investigated should be identified before the use of reaction probes. +

Aside these shortcomings the reaction probes offer even the opportunity to measure in liquid steel baths with temperatures more than 1500°C, which is currently not accessible with other technologies.

Figure 11.4.7. Modified two component drag reaction probe designed by [Moros, et al., 1985]

11.4.4 Hot wire anemometry (HWA)

Quite a lot of problems arise using hot film anemometers in liquid metal flows. The main question is the chemical compatibility of the liquid metal and the hot wire, in which surface tension and heat transfer aspects has to be considered. If alkali or earth alkali metals are used for the loop the compatibility of the wire with the liquid may become a killing issue, due to the low electrochemical potent of these liquids. Up to now only silicium oxide plated wires of hot wire anemometers shows no degradation in connection with NaK at temperatures up to 100°C, see [Reed, et al., 1986, 1987, 1989]. [Murthy & Szekely, 1983] went with Woods metal up 120°C, but nearly all other hot film measurements were restricted to mercury, gallium or other low melting liquid metals or alloys like in the papers by [Malcolm, 1969], [Hill & Sleicher, 1971], [Platnieks, 1971], [Sleicher & Lim, 1975]. Only one example of an application reaching a temperature of 250°C in Na^44 K^56 was found which was performed by [Hochreiter & Sesonske, 1969] and one for sodium up to 300°C by [Platnieks & Ulmann, 1984].

Surface effects which occur due to impurities in the liquid metal lead to reaction and change the characteristics of the probe. Only by an appropriate cleaning of the probe such an effect can be avoided. Another issue related to MHD has to be considered using hot wire probes. The hot wire probe measures in principle the heat transfer from the wire. The heat transfer in a MHD flow however is different to that of an ordinary hydrodynamic flow. The measurements of [Lykoudis & Dunn, 1973] show that the Nusselt number $Nu$ strongly depends on the Hartmann number $M$ or $Ha$ [see Eq. (2.6)] and the hydraulic Reynolds number (see Figure 11.4.8). Thus, a calibration measurement of the hot wire anemometer for each measured magnetic field strength has to be performed.
Figure 11.4.8. Dependence of the Nusselt number \( Nu \) on the Reynolds number \( Re \) and the Hartmann number \( M \) (or \( Ha \)) in a hot wire calibration measurement performed by [Lykoudis & Dunn, 1973]

In contrary to the potential probe the hot wire anemometer is not capable to detect the direction of the flow, because it measures the integral heat transfer at the wire, see e.g. [Hill & Sleicher, 1971]. So using this probe type correlation measurements, which are necessary to determine vortex structures in turbulent flows can not be performed. Another disadvantage of the hot film probes originates from the low Prandtl numbers of the liquid metal leading to a drastic reduction of the resolution of the probe, because the conductive heat transfer in liquid metals is favoured compared to the convective one. Hot wire probes type exhibit an interesting feature serving a crucial advantage compared to reaction probes and PMP sensors. They are rather small, the wires are only some microns thin which affects the flow hardly but the probe is on the other side not very robust. A schematic drawing of a HWA probe is shown in Figure 11.4.9.

Figure 11.4.9. Schematical drawing of hot wire anemometer
The high thermal conductivity of liquid metals plus the necessity of keeping a nearly constant temperature makes the use of HWA probes difficult. Another problem is a drift that may occur in the signal because of the disposition of oxide in metals that are easily oxidised by air. In [Szekeli, *et al.*, 1988] it is reported that despite protective blankets of inert gas it is common to encounter drift in the signal due to fouling of the probe by oxide in both mercury and Woods metal.

Another issue related to HWA probes is that the sensitivity of the probe is inhibited at low Peclet numbers. Here, even at quite low flow frequency oscillations the low Prandtl number of the liquid metals yield to a reduction of the signal, see [Malcolm & Verma, 1981]. The Peclet number is defined by the product of the Reynolds number with the Prandtl number in the way:

\[ Pe = Re \cdot Pr \quad \text{with} \quad Pr = \frac{v \rho c_p}{\lambda} \]  

where \( v \) is the kinematic viscosity in \([\text{m}^2/\text{s}]\), \( \rho \) the specific density in \([\text{kg/m}^3]\), \( c_p \) the heat capacity in \([\text{J/(kg K)}]\) and \( \lambda \) the heat conductivity in \([\text{W/(m K)}]\). For the observed decreasing sensitivity at low Peclet numbers two effects are responsible:

a) The amplitude of fluctuation is attenuated and the degree of attenuation depends upon a non-dimensional quantity \( \kappa \frac{fu^2}{u^2} \) in the range of Peclet numbers up to 10, where \( \kappa \) is the thermal diffusivity given by \( \kappa = \frac{\lambda}{(\rho c_p)} \), \( f \) the frequency of the fluctuations and \( u \) the mean flow velocity. The amplitude is attenuated by 10% and 90% at \( \kappa \frac{fu^2}{u^2} \) values of 0.02 and 4.0 respectively.

b) There is a phase lag in the HWA signal with respect to the true velocity of the fluctuation which is somewhat the same as that in potential flow at low frequencies, but it is considerably higher than that in potential flow at higher frequencies. The measured lag does not level off asymptotically at high frequencies.

11.4.5 Transition time methods

11.4.5.1 Temperature pulse method

The temperature pulse method is based on the measurement of the decay time of temperature pulses in a medium. The fluid velocity can be calculated from the propagation time of the temperature pulse. The temperature waves are produced by a miniaturised heater, which is surrounded in defined positions by thermocouples. The propagation of a temperature pulse in a fluid at rest is shown in Figure 11.4.10(a). A drawing of the measurement instrument is shown in Figure 11.4.10(b). A problem may arise with this measurement method in fluids with extremely low Prandtl numbers like in liquid metals, because there a temperature pulse diffuses rather fast. Therefore, high temperature pulses have to be brought in the liquid metal in order to enable a resolvable measurement of temperature changes in small distances from the miniaturised heater. A determination of the velocity vector is only possible if a grid of thermocouples is placed next to the heater. Such a grid affects the flow non-negligibly, however. A second aspect which should be also considered is the choice of the thermocouples for this method, see therefore Section 11.6. [Casal & Arnold, 1988] demonstrated the viability of this measurement method in water and also in liquid metals. Nevertheless, the resolution of this method in liquid metals is rather poor around \( \pm 25\% \) and the technical effort high.
11.4.5.2 Tracer studies

Tracer studies were initially developed for velocity and diffusivity measurements in molten salts. In using this technique a small amount of tracers is introduced at a defined time $t$ at a discrete point of the flow field, while downstream the liquid is sampled periodically. A simple representation of this technique is sketched in Figure 11.4.11(a). If the integrity of the tracer is ensured for the duration of the experiment and assuming isotropic conditions the tracer concentration $C$ in a radial co-ordinate system is given by Eq. (11.32).

$$\frac{\partial C}{\partial t} = \frac{D_t}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right)$$  \hspace{1cm} (11.32)

where $D_t$ is the molecular diffusivity in case laminar flows or the effective diffusivity considering turbulent flows. In principle the tracer studies are a coupled initial and boundary problem so that for assuming the following conditions:

$$C = 0 \text{ at } r \to \infty; \quad C \text{ finite for } t > 0, \text{ at } t = 0 \quad C = \delta(t = 0)$$  \hspace{1cm} (11.33)

The solution of Eq. (11.32) under the conditions (11.34) is given by:

$$C = \frac{A}{2\sqrt{\pi} D_t^3} \exp \left(-\frac{r^2}{4D_t t} \right)$$  \hspace{1cm} (11.34)

where $A$ is a constant. However, for a moving co-ordinate system the location $r_{\text{Sensor}}$ of the sampling sensor is given by $r_{\text{Sensor}} = d - ut$, where $u$ is the probe flow velocity so that Eq. (11.34) mutates to:

$$C = \frac{A}{2\sqrt{\pi} D_t^3} \exp \left(-\frac{(d-ut)^2}{4D_t t} \right)$$  \hspace{1cm} (11.35)

By fitting the measured concentration curve [Figure 11.4.11(b)] to Eq. (11.35) the quantities $u$ and $D_t$ can be determined. There are problems arising from the above interpretation with the path pursued.
by the fluid between the point where the tracer was introduced and the sampling point, the tracer decay, while the velocities measured in this way are average values over a relatively large region. Velocity and diffusivity measurements are reported by [Grjotheim, et al., 1970, 1971] and [Berge, et al., 1973] for aluminium reduction cells. Tracers may not only be oxides of the fluid investigated but also radionuclides can be used, as suggested by [Szekely, 1964] and [Szekely & Chang, 1977a,b].

The tracer methods allow to measure even in steel and iron bath but its accuracy is rather poor and a lot of pre-knowledge of the velocity in the domain of interest is required. In all cases measurements and theoretical predictions agreed within a factor of ±50%.

11.4.5.3 Dissolution studies

Measurements of metal velocities from the mass lost of iron rods introduced in liquid aluminium were initially developed by [Johnson, 1978] and subsequently improved [Taberaux & Hester, 1984]. The latter derived calibration curves correlating mass loss with liquid metal velocity by measuring the iron rod mass lost in a stirred tank using a load cell. Here the following correlations are used:

\[ Sh = A + B \cdot Re^n \cdot Sc^m \]  
\[ \beta \cdot \frac{d}{D_i}, Re = \frac{u \cdot d}{v} \text{ and } Sc = \frac{v}{D_i} \]

\( \beta \) is the mass transfer coefficient and is not a material property. It depends on the concentration, velocity and temperature field and has the dimension of the velocity. The analogue of the Sherwood number in heat transfer problems is the Nusselt number. Thus, the Sherwood number is often called the Nusselt number of the mass transfer.

Due to the dependence of the mass transfer coefficient \( \beta \) on flow, concentration and temperature field a sophisticated calibration procedure is required which is described in detail by [Bradley, et al., 1984]. Besides aluminium this methods has been also applied to steel melts by [El Kaddah, et al., 1984]. By determining the extend of dissolution for specific time intervals, the local mass transfer coefficients are calculated and compared to the predicted ones using both laminar [Eq. (11.38)a] and turbulent correlations [Eq. (11.38)b], which were found experimentally by [Grevet, et al., 1982] and [Szekely, et al., 1984].
Herein, $Tu$ is the turbulence intensity. $Tu$ and $Re$ were an input to the above named correlations from a numerical simulation. A clear analysis of the relations (4.38)a,b rapidly exhibits that both of them has an error of about $\pm 25\%$, see e.g. [Jischa, 1982].

### 11.4.6 Neutron radiography

The attenuation of neutron rays for heavy liquid metals is small. Therefore, the flow in these liquid metals can be seen by neutron rays. An initial method to visualise the flow a liquid metal by tracer and dye injection using the neutron radiography has been made by [Takenada, et al., 1994]. They used an accelerator-based real-time neutron radiography. In these first studies a fluorinated hydrocarbon which is transparent for neutrons was used. For the use in heavy liquid metals, however particles owing a similar density are required. [Takenada, et al., 1996] report that for the use in eutectic lead-bismuth gold cadmium (AuCd$_3$) intermetallic alloy particles were successfully applied, since they wet well by this liquid and its density is close to that of the metal. The flow can be visualised by watching the movement of the individual particles by real-time radiography and a digital image post-processing procedure.

The image post-processing method used is the same as for the particle image velocimetry (PIV), in which the acquired images of the moving tracers are obtained by subtracting the time averaged image from the original one. With two consecutive images of the moving tracer, pattern matching is carried out at each point to obtain the flow vector by calculating the spatial correlations. Since the tracers are much larger than one image element, i.e. that of noises in the experiment, the image of the tracers can be easily obtained by using a spatial filter in the image processing program. Because the noise is random and has no correlations, the noise does not affect the spatial correlation of the tracer signals. The spatial correlation function $\Psi(u,v)$ between the data of two consecutive images $f_1(x,y)$ and $f_2(x,y)$ is defined as:

$$\Psi(u,v) = \iint f_1(x-u, y-v) \cdot f_2(x,y) \, dx \, dy$$

(11.39)

With this method Takenada, et al. achieved temporal resolution of 30 Hz. The most probable movement of the tracers pattern is indicated by $(u,v)$ at the peak of the function and the flow vector can be determined. Since the noises are random, the spatial correlation method is applicable to the images where the tracer and the noise can not be divided by any spatial filters. Reasonable vector fields with an uncertainty of less than 10% could be obtained in lead-bismuth eutectics, the thickness of which is 25 mm, i.e. the attenuation rate is about $1/e$, by the spatial correlation method even if the tracer sizes were the same order as those of the image noises. Since the attenuation coefficients of sodium and sodium-potassium are much smaller than that of lead-bismuth, flow in thick liquid metal layers of alkali metals can be visualised.

### 11.4.7 Fibre mechanics systems (FMS)

The measuring apparatus of FMS is based like the reaction probe on simple mechanics in the way that a mechanical sensor, which is in direct contact with the hot liquid, is mounted rigidly on an optical system used to acquire the measuring data. The thin tip of the probe shaped by a special glass manufacturing technique in form of a cone acts as sensitive part. A small glass rod, the so-called pointer having a length of order 10-50 mm, depending on the desired sensitivity of the probe is positioned...
inside this glass tube and connected with the sensor tip ideally only at the front point. Technically it is bonded mostly over a length of 1 mm. The initial position of the free end of the pointer is approximately located in the centre of the glass tube. In presence of a fluid motion around the tip the sensor reacts in form of an elastic deformation as shown in Figure 11.4.12(a). Consequently, at the opposite end a resulting spatial shift of the pointer can be observed by optical means in the opposite direction to the displacement of the sensor tip. The deflection of the tip is a function of the fluid velocity at the tip. The evaluation of the direction and the amplitude of the pointer displacement allow to determine the two velocity components perpendicular to the sensor. Therefore, an endoscope combined with a lens system connected to a CCD array is used to observe the pointer image. By digitalisation and analysing of the images using a frame grabber the informations are stored.

Figure 11.4.12. (a) Measurement principle of a mechano-optical probe. (b) Stereo-microscopic photograph of a mechano-optical probe with an attached sphere by [Eckert, et al., 2003]. (c) Mechanic model of the displacement of the probe tip by the flow to evaluate the flow velocity.

Initially such systems were invented by [Zhilin, et al., 1987, 1989] and [Boyarevich, et al., 1990]. But, a higher resolution and a successful miniaturisation and implementation to higher melting point liquids were reached by [Eckert, et al., 2000]. They managed to fabricate probe tips with diameters around 50 μm and embedded pointers with a length of 30-40 mm. The bonding of tip and sensor was only 1 mm, which represents the integration length scale of the sensor in the flow.

A critical point is the choice of the sensor material. The material has to obey Hooks law and must be temperature and chemical resistant to the fluid of interest, e.g. boronsilicate glass is favourable for applications up to 350°C in sodium, gallium but also InGaSn, SnPb, SnBi or PbBi. It exhibits a constant elastic modulus \( E \) up to 400°C, see [Scholze, 1965] and is even stable against sodium (compare [Eckert, 1997]). Moreover, the fabrication technology and handling of this glass type is simple. For higher temperatures quartz-glass tips can be used, which operate up to temperature of 800°C, see [Eckert, et al., 2003].

In order to calculate the pointer displacement the sensor tip is considered as a mechanical element in the configuration shown in Figure 11.4.12(c). A flow around the tube causes a more or less constant force per unit length \( f = \rho \ r \ u^2 \ C_w \) leading to a deformation of the sensor, where \( r \) is the radius of the tube and \( f \) its length, \( r \) the specific fluid density, \( u \) the velocity and \( C_w \) the drag coefficient. The displacement of the tube from the equilibrium position is described by the parameter \( h(z) \).
Assuming that the tube is bent by a torque \( M_x \) in \( x \)-direction the displacement is expected parallel to the \( y \)-direction. The original \( x-z \)-sections are not deformed and remain transverse to the \( y \)-axis. If we consider only small displacements \( h(z) \) and the wall thickness \( \delta \) is small compared to \( r \) then the moment of inertia transverse to the tube \( I_x \) can be approximated by \( I_x = \pi \delta r^3 \). Thus, one obtains an ordinary differential equation for the force \( f \) in the form:

\[
f = \frac{d^2 M_x(z)}{dz^2} = E \cdot I_x \cdot \frac{d^4 h(z)}{dz^4}
\]

where the elastic modulus \( E \) and the moment of inertia in \( x \)-direction \( I_x \) are assumed to be constant. Imposing the boundary conditions \( h = (dh/dz) = 0 \) at \( z = 0 \) and \( M_x = (dM_x/dz) = 0 \) at \( z = l \) one obtains:

\[
h(z = l) = \frac{C_w \rho u^2 l^4}{8E \pi^2 \delta}
\]

According to the drag curve for a flow around a cylinder, see [Brauer, 1971] the \( C_w \) value can be considered as constant in a wide range so that a parabolic dependence of the measured quantity \( h(z) \) can be expected. A significant influence of the probe geometry in terms of \( r, l \) and \( \delta \) becomes obvious, which allows a defined adjustment of the sensor with respect to the desired velocity range.

An enhancement of the sensitivity can be obtained by attaching a sphere to the sensor tip, see also Section 11.4.3. If the radius of the sphere \( r_s \) is significantly larger than the fibre shaft the bending is mainly governed by the sphere at the end of the fibre. Thus, the boundary conditions applied to Eq. (11.40) are \( h = (dh/dz) = 0 \) at \( z = 0 \) and \( M_x = 0 \), \( (dM_x/dz) = -F_s \) at \( z = l \), where \( F_s \) is the force acting on the sphere, which yields:

\[
h(z = l) = \frac{C_D \rho r_s^2 u^2 l^3}{6E \pi^3 \delta} \quad \text{with} \quad F_s = \frac{\pi}{2} C_D \rho r_s^2 u^2
\]

Since the drag coefficient of a sphere \( C_D \) is even less sensitive to the Reynolds number than that of the tube, i.e. it is almost constant for \( 10^2 < Re < 3 \times 10^5 \) an increase of the sensitivity of a factor three can be attained. Such a sensor type is shown in Figure 11.4.12(b).

To extract the actual velocity from the measurements each sensor tip has to be calibrated separately. Due to the dependence of the pointer displacement on the fluid density the calibration procedure has to be performed with the same liquid as the later on conducted experiment.

### 11.4.8 Pitot and Prandtl tubes

#### 11.4.8.1 General features and application

The measurement principle of Pitot and Prandtl tubes was already explained in Section 11.2.3.2 in the context of the flow rate measurement. Thus only some remarks on the operational experience are made. Via miniaturisation of the sensors local velocities and if thermocouples are embedded heat fluxes can be measured. The resolution of this local measurement technique is given by the resolution of the used pressure gauges.

The THESYS loop of KALLA, which uses Kulite pressure transducers, could determine the local velocity with an accuracy of 5 mm/s. The Pitot tube used there is sketched in Figure 11.4.13(a) and is
capable to resolve a pressure of 12.5 Pascal. Higher resolutions may be obtained by more sensitive sensors. A typical turbulent velocity profile and the corresponding temperature profile which has been measured by means of a combined Pitot tube with two thermocouples in a circular tube at a temperature of 300°C with a Pitot tube is depicted in Figure 11.4.13(b).

Figure 11.4.13. (a) In KALLA developed Pitot tube with small thermocouples to measure local velocities \(u(z)\) and temperatures \(T(z)\) and their fluctuations. (b) Measured mean velocity and temperature in a turbulent lead bismuth pipe flow at 300°C with the Pitot tube depicted in (a).

The smallest spatial dimension over which the velocity is integrated, is given by the size of the orifice of the Pitot tube. As the surface tension of heavy liquid metals like lead or lead-bismuth is quite large and of order \(O(10^2 \text{ mN/m})\) the pressure difference required to fill the tubes orifices significantly increases with the degree of miniaturisation. A reliably operating Pitot tube system is only obtained for a gas free tube. Thus, drain tubs to ensure a complete filling of the sensor are required. Due to the large Reynolds numbers appearing in HLM flows the boundary layers appearing there are relatively thin and thus only near to the region towards the main flow resolvable with Pitot tubes. An experimental example of the flow field measurement using a Pitot tube near a heated rod in an annular cavity is shown in Figure 11.4.14. In order to acquire the flow distribution within the boundary non-intrusive methods are required as the ultrasound Doppler velocimetry (UDV).

Figure 11.4.14. Measured mean velocity \(u_z [\text{m/s}]\) near a rod in an annular cavity as a function of the radius \(r [\text{mm}]\) at \(T_{in} = 300^\circ\text{C}\) for different Reynolds numbers \(Re\) at \(z/d = 13.9\) from [Lefhalm, et al., 2004]
In order to obtain accurate mean velocity profiles using a Pitot tube many corrections need to be made to account for the effects of viscosity, turbulence, velocity gradients and the presence of a wall. Recent measurements by [Zagarola and Smits, 1998] in a turbulent pipe flow in a Reynolds number regime from $3.1 \times 10^5 < Re < 3.5 \times 10^7$ have raised questions regarding the accuracy and applicability of the current correction methods, which are summarised in the work of [Perry, et al., 2001]. In pipe flows with Reynolds numbers around $10^5-10^6$, which easily appear in heavy liquid metal applications, there is a difference of greater 5% in the slope of the logarithmic region between data with and without wall correction [McKeon, et al., 2003].

### 11.4.8.2 Viscous corrections for Pitot tubes

Viscous corrections are important if the Reynolds number based on the probe diameter, $Re_d$, falls below $10^3$. This is one of the most important – and most often forgotten – corrections while using Pitot tubes. If the Reynolds number $Re_d$ is larger than $10^3$ the viscous correction is in the range of 0.5% [Zagarola, 1996]; for smaller values of $Re_d$, however, it can reach several %. Using the pipe flow results from [Barker, 1922], [Reichardt, 1951], [Hurd, et al., 1953], authors [MacMillan, 1954, 1956], [Chue, 1975] and [Zagarola, 1996] suggested that for $Re_d > 30$ the following relation should be applied:

$$C_p = 1 + \frac{10}{(Re_d)^{\frac{1}{2}}}$$  \hspace{1cm} (11.43)

where $C_p$ is the measured pressure coefficient. Due to the numerous experimental data Eq. (11.43) can be considered as a true representation of the viscous effects on the Pitot tube data.

### 11.4.8.3 Turbulence correction for Pitot tubes

The effects of turbulence on the Pitot tube reading are two-fold. First, the velocity fluctuations increase the measured pressure. Second, when measurements are taken using a pressure tapping at the wall to measure the static pressure, the radial gradient in static pressure due to velocity fluctuations must be taken into account. The combined effect of these two phenomena is given by [Ozarapoglu, 1972] by:

$$\frac{u - u_m}{u_m} = \frac{\overline{u^2} - (1 + K_t)\overline{v^2} + (1 + K_r)\overline{w^2}}{2u_m^2}$$  \hspace{1cm} (11.44)

where $u$ is the true mean velocity, $u_m$ is the measured mean velocity and $\overline{u^2}$, $\overline{v^2}$ and $\overline{w^2}$ are the mean square velocity fluctuations in the streamwise, radial and circumferential directions. $K_t$ is a coefficient that accounts for the directional sensitivity of the Pitot probe and is for circular taps around 0.3. While measuring close to the wall [Dickinson, 1975] suggested that for $y^+ > 50$ Eq. (11.44) could be simplified in the way:

$$\frac{u - u_m}{u_m} = \frac{\overline{v^2}}{2u_m^2}$$  \hspace{1cm} (11.45)

accepting errors of ±0.5%. Here, the dimensionless wall distance $y^+$ is defined as:
\( y^* = \frac{\Delta y \cdot u_t}{v} \) where \( u_t = \sqrt{\tau_\infty / \rho} \) (11.46)

\( u_t \) is the friction velocity, \( \Delta y \) is the wall normal distance from the wall, \( \tau_\infty \) the wall shear stress and \( \rho \) the specific fluid density and kinematic viscosity.

### 11.4.8.4 Velocity gradient correction for Pitot tubes

In a shear flow the presence of the probe deflects the streamlines so that the probe registers a velocity that is higher than the velocity at the geometric centre of the probe. In order to account for this interference effect, which usually dominates all other Pitot tube errors, a correction is made which can be expressed as an error in the measured velocity or as an apparent shift in the probe location. The origin of this error is schematically shown in Figure 11.4.15.

**Figure 11.4.15. The effect of a Pitot tube on the streamline pattern; left in a shear flow and right in a uniform flow near a wall without adhesive wetting \( u \neq 0 \) but \( v = 0 \)

If the velocity gradient across the Pitot tube is small compared to its mean value and additionally if we assume that the mean velocity is a function of \( y \) only then one can deduce:

\[
\frac{\Delta u}{u(y_c)} = \frac{u(y_c + \Delta y) - u(y_c)}{u(y_c)} = 2 \alpha \frac{\Delta y}{d}^2 \cdot \beta \left( \frac{\Delta y}{d} \right)^2 + \ldots
\]

(11.47)

where \( y_c \) is the position of the centre of the Pitot tube, \( u(y_c) \) is the true velocity at \( y_c \), \( \Delta y \) is the correction in the position due to the streamline displacement and the velocity gradients are evaluated at the centre of the probe. \( d \) is the diameter of the probe. The coefficients \( \alpha \) and \( \beta \) are defined by:

\[
\alpha = \frac{d}{2u(y_c)} \left. \frac{du}{dy} \right|_{y=y_c}, \quad \beta = \frac{1}{2} \left. \frac{d^2 u}{dy^2} \right|_{y=y_c}
\]

(11.48)

Eq. (11.47) exhibits that the correction in the velocity and the apparent shift of probe position \( \Delta y/d \) are directly connected. In fact, the velocity gradient correction is usually implemented by correcting the probe position rather than by correcting the velocity itself. This form is often called the displacement correction and several authors like [MacMillan, 1954], [Livesey, 1956], [Patel, 1965] [Tavoularis & Szymczak, 1989] have suggested that:

\[
\frac{\Delta y}{d} = \varepsilon
\]

(11.49)

where \( 0.08 < \varepsilon < 0.16 \). Other correction correlations for individual applications can be found in the paper by [Chue, 1975] and [Patel, 1965] or [Zagarola & Smits, 1998].
In the presence of a wall, there is an additional mechanism for streamline displacement. Consider a Pitot tube resting on the wall in a uniform flow, as shown in Figure 11.4.15 right. Since it resembles a forward-facing step, it may be expected that the streamlines would be displaced away from the wall, that is towards the region of higher velocity (rather than towards the region of lower velocity as it is in free shear). Therefore, the true correction close to the wall must be some combination of these two effects. Already [MacMillan, 1956] observed this trend and suggested that a wall correction was necessary in addition to the displacement correction for \( \frac{y}{d} < 2 \). He proposed that this wall correction may be represented by:

\[
\frac{\Delta u}{u} = 0.015 \exp\left[-3.5\left(\frac{y}{d} - 0.5\right)\right] \tag{11.50}
\]

It should be noted in this context that the MacMillan corrections were not corrected for the effects of turbulence intensity and velocity gradient. In other words, implementing an additional turbulence correction when using the MacMillans method is not appropriate.

### 11.4.8.5 Displacement correction for Pitot tubes

The displacement correction is another type of velocity gradient correction, which is more accurate. Best results have been obtained by [McKeon, et al., 2003] using the following relation:

\[
\frac{\Delta y}{d} = 0.15 \cdot \tanh\left(4 \sqrt{\alpha}\right) \tag{11.51}
\]

where \( \alpha \) is defined by Eq. (11.48). This form is based on the analysis by [Hall, 1956] and [Lighthill, 1957], who found that the displacement correction for a sphere in a velocity gradient could be expressed by a hyperbolic tangent function of the non-dimensional shear. The constants described by [McKeon, et al., 2003] matches experimental data based on the analytical derivation of [Hall, 1956] in such a way that both collapse identically. Note that this type of correction gives zero displacement for zero shear and asymptotes the [MacMillan, 1956] correction for large shear, i.e. \( \alpha \to 1 \).

### 11.4.8.6 Wall correction of Pitot tubes

The wall correction based on the Preston tube data of [Patel, 1965] was made under the condition where the probe is under maximum influence of the wall as well as shear. Where a Preston tube is simply a Pitot tube resting on the wall. If one assumes that the Preston tube reads the true pressure at:

\[
y = 0.5 \cdot d \left(1 + \frac{\delta_w}{d}\right) \tag{11.52}
\]

then a definition of the wall displacement correction \( \delta_w \) is obtained. If the form of the velocity profile is known, \( \Delta \rho_0 = \frac{1}{2} \rho u^2 \) may be formulated and substituted in the expression of the logarithmic low for the boundary layer velocity distribution.

Especially for \( 8 < d^* < 110 \) viscous effects are undoubtedly important, and its known that \( \alpha \) changes significantly, so that one can expect that \( \delta_w \) will vary with \( d^* \). [McKeon, et al., 2003] elaborated the following wall corrections applicable for \( y/d < 2 \):

520
11.4.8.7 Comments on displacement and corrections

To evaluate displacement and wall corrections it would be convenient if the true velocity profile was known. Unfortunately, the nature of the true profile is still a source of debate, specifically as to what role geometry and/or Reynolds number play, particularly in the buffer region. To clarify this aspect, experimentally non-intrusive methods like LDA in transparent fluids and UDV in opaque ones as well as direct numerical simulations, see e.g. [Eggels, et al., 1994] lead to a further insight.

11.5 Void fraction sensors

In the concept for an accelerator-driven system (ADS) the injection of gas is considered as a method to generate a natural convection inside the liquid metal loop. In order to control the flow rate of the liquid metal and the resulting pressure drop the structure of the two-phase flow in the riser has to be known. Besides the description of the integral state of a two-phase flow, which is described of by the void fraction the local conditions are of interest. Therefore, measurement equipment is required to measure locally the void fraction, the bubble size and the individual transport velocities.

Like for the local measurement methods the application of intrusive and non intrusive methods can be applied also in liquid metals. Intrusive methods are e.g. the local resistive probes, while a non-intrusive sensing can be achieved by means of X-ray (γ-ray) techniques, neutron radiography (NR) or the ultrasound Doppler velocimetry (UDV). Due to the opaqueness of the fluid optical or fibre optical methods can not be used. The high specific electric conductivity of liquid metals does not allow the use of impedance probes, because hardly any electric field of significant size can be built up within the fluid, see [Cho, et al., 2005]. In bad electrically conducting media sometimes the magnetic resonance imaging (MRI) is used, which requires considerable large permanent magnetic [Daidzic, et al., 2005]. However, the interaction of the magnetic field with the fluid motion yields Lorentz forces altering the flow pattern and void distribution within the duct in such a way, that the intended measuring quantity is hidden behind the magneto-hydrodynamic effects.

The consecutive chapter describes the techniques successfully applied to liquid metals so far its operations principles and its deficits. It starts from the global methods acquiring the void fraction within a defined cross-section and continues with the individual devices measuring the local effects. In contrast to the single-phase investigations the information about two-phase liquid metal flow instrumentation is rather sparse. Nevertheless, the author tries to present the currently available technologies and discusses its limitations.

11.5.1 Electromagnetic sensors

An exact description of the characteristics of two-phase flow is required for better performance and safety design of power plant and air-conditioning machinery. In general, it is not easy to measure simultaneously the liquid volume flow rate and the void fraction under the existence of a gas phase. The electromagnetic flow-meter has been used successfully and accurately to measure the mean liquid velocity in various industries for about 40 years.

\[
\frac{d\gamma}{d} = \begin{cases} 
0.150 & \text{for } d^+ < 8 \\
0.120 & \text{for } 8 < d^+ < 110 \\
0.085 & \text{for } 110 < d^+ < 1600 
\end{cases}
\]
The electromagnetic flow meter is a device for detecting the potential difference between electrodes that is induced when a conducting fluid flows through a magnetic field, see e.g. Section 11.2.1. The feasibility of using the electromagnetic flow meter for measuring the characteristics of two-phase flow has been continuously considered. The reasons for this are that it makes no pressure drop, it has fast response for the change of flow, and it can effectively use the sharp difference between conductivities of two phases. There are many potential applications for the electromagnetic flow meter in two-phase flow, but uncertainty due to the effects of the non-conducting phase also exists. As for electromagnetic flow meters, generally two types of electromagnetic void fraction sensors can be used: the DC permanent magnetic sensors and the AC sensor types. Both are described below.

11.5.1.1 DC permanent magnet void fraction sensors (PMVS)

The permanent magnet void fraction sensors (PMVS) rely on the same principle as the DC permanent magnetic flow meter (PMF), presented in Section 11.2.1.1. Also the experimental set-up is the same, consisting of a permanent magnet imposing a steady magnetic field $B$, penetrating the geometry to be investigated. The electrodes are arranged both perpendicular to flow $u$ with $u_f$ and $u_g$, and the magnetic field $B$, where $u_f$ is the mean fluid velocity and $u_g$ the mean velocity of the gas. Further on the subscripts “$f$” and “$g$” denote the fluid and the gas, respectively. Since liquid metals possess a high specific electrical conductivity being order of magnitude larger than that of its vapour or the one of other gases one can assume that to the leading order the signal output of a PMVS will be a linear function of the liquid velocity alone up to a high value of vapour volume fraction. This postulation, however, assumes that at least to the temporal mean a uniform current path is maintained normal to the liquid metal flow.

The flow of a two-phase stream may be expressed as:

$$m_f = \rho_f A (1 - \alpha) u_f$$  \hspace{1cm} (11.54)

where $\alpha$ represents the gas volume fraction, $m_f$ the mass flux and $A$ the ducts cross-section. The ratio $u_f/u$ is obtained from Eq. (11.55)a and the total mass flow $m$ is equal to sum of the gas and liquid flows as in Eq. (11.55)b.

$$\frac{u_f}{u} = \frac{m_f}{m} (1 - \alpha), \quad m = m_f + m_g$$  \hspace{1cm} (11.55) \hspace{1cm} a,b

Defining the quality $x$ as $x=m_f/m$ one gets:

$$\frac{u_f}{u} = \frac{(1 - x)}{(1 - \alpha)}$$  \hspace{1cm} (11.56)

Considering now only low qualities in the range $0 < x < 0.02$, Eq. (11.56) mutates to:

$$\alpha = 1 - \frac{u}{u_f}$$  \hspace{1cm} (11.57)

in which $u$ and $u_f$ can be independently measured by permanent electromagnetic flow meters; one in the two-phase domain as $\Delta \phi$ and the second in the single phase flow $\Delta \phi$. Connecting both readings one gets directly the void fraction from:
where $k_f$ and $k$ are the calibration constants of the single and the two-phase electromagnetic flow meters. In alkali liquid metals this technique has been successfully proofed by [Heinemann, et al., 1962]. In their tests the compared the PMVS experimental data with $\gamma$-ray measurements and they obtained an accuracy of this method of $\pm 5\%$ up to void fractions of 66% and temperatures of 600°C. However, the claimed that a high temperature wetting procedure was necessary to ensure constant thermal-electric properties at the fluid wall interface, unless a reliable reading could not be achieved. Also for mercury as a representative of a high density liquid metal this technique has been successfully demonstrated by [Hori, et al., 1966]. In case of well electrically wetting fluids this technique has been improved by [Ochiai, et al., 1971].

Additional correction factors for a more accurate detection of the void fraction value were made by [Murakami, et al., 1990]. Correlation techniques to acquire high temporal resolutions were made by [Velt, et al., 1982]. However, the latter three works concentrated mainly on the use in alkali metals.

### 11.5.1.2 AC electromagnetic void fraction sensors (EMVS)

A method to overcome the problems of direct wetting of the surface is given by AC sensors, similarly as for the flow meters. In Figure 11.5.1 an EMVS invented and successfully tested by [Cha, et al., 2002] is shown.

**Figure 11.5.1.** (a) Schematic drawing of the EMVS used by [Cha, et al., 2003].
(b) Normalised output of electromagnetic flow meter considering the ratio of correction factor with void fraction $\alpha$ after [Cha, et al., 2003].

Within their device the electromagnet of the electromagnetic flow meter is sinussoidally excited and controlled by a frequency converter and an uninterruptible power system. The flow meter is composed of a signal detector and a signal processor. A pair of corrosion-resistive and non-magnetic electrodes is mounted along the inner wall of the test tube. Lead wires to draw out the signal are connected at both electrodes, and shielded for noise proofing, with the shield lines being grounded at one end. One of the greatest difficulties in electromagnetic flow meter design is that the amplitude of the voltage across the electrodes is of the order of a few millivolts, which is relatively small compared with extraneous voltages and noise. The main noise sources of electromagnetic flow meters, excited by AC power, are as follows:
the transformer signal from the alternating magnetic field (including the effect of eddy current in the flow tube);
noise from the capacitive and resistive coupling between signal and power circuits.

The following effects that distort the signal (flow signal) corresponding to flow rate should be noted:

- fluctuation of the magnetic field due to fluctuation of the power input;
- iron loss and hysteresis effects of the electromagnet;
- amplifier loading effect from the impedance of measuring devices.

To avoid the difficulties stated above, a somewhat complex signal processing unit was needed. The signal processor has an input stage with voltage followers, a filtering stage and an amplifying stage with large gain (> 10^2). To cancel out the differential noise (transformer signal), a counter differential noise is generated intentionally before the voltage followers with a kind of pickup coil and variable resistor. Low-frequency excitation using a frequency converter enables to reduce the noise by capacitive and resistive coupling between the signal and power circuits. Using these procedures, noise can be reduced considerably, and zero-flow tuning is possible. A reference resistor is used to ensure the reference voltage must have the same phase as the excitation current. From the reference voltage, information about the characteristics of the magnetic field can be inferred, and the comparison between flow signal and noise is possible.

Further, the EMVS requires a single-phase calibration procedure to determine the calibration constants. In fact, the void fraction can not be measured directly with one device in the liquid metal/gas system. By using two EMVS an artificial void fraction can be calculated from the signals of the two electromagnetic flow meters under the assumption that the ratio of correction factors of both flow meters is unity, similar as for the DC flow meters. For the single-phase flow calibration of each of the devices, the correction factors can be determined. As a result from both calibrations one gets a linear dependence of the signal ratio versus the void fraction for low void fractions up to \( \alpha = 0.3 \). However, this signal ratio is not the actual real void fraction value since the ratio of correction factor is not unity: It is a function of fluid conductivity and hence is coupled to the void fraction. The effective conductivity \( \sigma_{eff} \), however, can be calculated by the correlation experimentally determined by [Petrick & Lee, 1964] and thus the signal ratio can be corrected to obtain the real void fraction. The result obtained by [Cha, et al., 2003] for a sodium-nitrogen system showed an uncertainty of less than 2%. The result is shown in Figure 11.5.1(b).

\[
\sigma_{eff} = \frac{(1-\alpha)^2}{1+\alpha} \sigma_f \quad \text{for} \quad 0 \leq \alpha \leq 0.7. \quad (11.59)
\]

### 11.5.2 X-ray, \( \gamma \)-ray and neutron radiography (NR)

The attenuation of various radiations has been used quite successfully by different experimenters since the late fifties [Hooker & Popper, 1958] or [Petrick & Swanson, 1958]. Nearly all of them have been applied to light metals previously considered for the fast breeder research. The growing interest of the metal casting industry as well as the transmutation of minor actinides put the focus on heavy liquid metals, which require strong source due to the large absorption. In the past decade these sometimes continuously-operating high power sources became available [Baker & Bonazza, 1998], [Satyamurthy,
et al., 1998], [Mishima, et al., 1999] or [Saito, et al., 2005]. An additional support in using the below described techniques came due to the improved computer technologies and the progress in the image processing algorithms.

11.5.2.1 X-ray absorption

This subsection describes the technique developed for visualisation of the multi-phase mixture and the transient measurement of the two-dimensional distribution of chordal averaged void fraction applicable to liquid metal gas two-phase systems. X-rays have been used successfully in the visualisation of vapour explosion phenomena and the measurement of void fraction by several authors. One example of the use of a flash X-ray source is the visualisation of the fragmentation process in single droplet vapour explosions by [Ciccarelli & Frost, 1994]. A recent use of flash X-rays to measure void fraction was the study of hot particles plunging into water by [Theofanus, et al., 1994]. But the use of a continuous source of X-rays for the measurement of void fraction in molten metal systems with gas is still seldom. First successful attempts in the system tin gas were made by [Baker & Bonazza, 1998]. Since this is still the standard it is described more extensively.

The imaging through a layer of heavy liquid metal and an additional structural material e.g. steel requires a high energy beam and a high dose rate to get data that can be used in quantitative analysis. [Baker & Bonazza, 1998] used for a 100 mm tin layer ($\rho_{\text{tin}} \approx 7 \times 10^3 \text{ kg/m}^3$) and 25 mm steel walls a continuous spectrum X-ray source with a peak energy of 9 MeV and an on-axis dose rate, one meter from the source, of 30 Gy/min to image the test section. The X-ray source pulses at approximately 275 Hz at this dose rate. The pulse frequency may be synchronised with the imaging system so that a constant number of one to nine pulses is collected for each frame. In most cases the X-ray and imaging systems are left unsynchronised to avoid a serious noise component introduced in the video signal.

The focal spot for the Baker-Bonazza (1998) X-ray source is less than 2 mm. The X-ray head is mounted on a scissor lift table that allows it to be moved vertically and aligned with the image collection system. Images are collected using an X-ray sensitive glass screen. The conversion screen is imaged through a mirror and a lens onto an inverting image intensifier which is coupled to one of two CCD cameras by means of a relay lens. Then the images are digitised and stored with a frame grabber. The signal path is shown in Figure 11.5.2(a).

Figure 11.5.2. (a) Arrangement of a void fraction measurement using the X-ray technique and the associated image recording. (b) X-ray image of gas injection at a rate of 9.2 cm/s into 11 kg of molten tin at 421°C. The top edge of the molten tin pool is clearly visible from [Baker & Bonazza, 1998].
The first step to obtain a digital image is to eliminate the effect of the CCD camera’s dark current. In a next step the images are normalised against any spatial non-uniformity of the X-ray source output. In the third step the images have to be normalised against any spatial non-uniformity originating from the structure of the test section. All these steps are achieved by means of subtracting a dark current constant $D$ from each pixel value $P(x,y)$, and by dividing this difference by the difference between the corresponding pixel value of an image of the empty test section (obtained immediately prior to the pouring of molten liquid metal into the test section), $P_0(x,y)$, and the same dark current constant, $D$. The logarithm of this ratio is a grey level from here on indicated as $P_{\text{liquid}}(x,y)$.

$$P_{\text{liquid}}(x,y) = \ln \left( \frac{P(x,y) - D}{P_0(x,y) - D} \right) \quad (11.60)$$

Due to the exponential nature of the interaction of the X-rays with material, $P_{\text{liquid}}(x,y)$ is directly proportional to the thickness of the absorbing material in the test section as described below. Since the production of secondary radiation from the test section structure is small, this technique also accounts for the attenuation that occurs in the structure of the test section. The value of each pixel in the subtracted image is dependent on the material; the X-ray beam must traverse when travelling from the source to the X-ray sensitive, glass screen. At an average energy of approximately 3 MeV, water, water vapour, and nitrogen gas are undetectable and the intensity $I$ of the pixel (gray level) is only dependent on the amount of liquid metal in the beam path and the magnitude of scatter present in the imaging plane. This relationship, where the liquid metal thickness, $z_{\text{liquid}}$, is the product of the liquid metal density and the portion of the chordal path length comprised of the liquid metal, is:

$$\frac{I}{I_{\text{empty}}} = B \exp \left[ -\left( \frac{\mu}{\rho_{\text{liquid}}} \right) z_{\text{liquid}} \right] \quad (11.61)$$

where $I$ is the X-ray fluence intensity in photons per square centimetre, $B$ the built-up factor, $\mu$ the magnetic permeability $4\pi \times 10^{-7}$ As/(Vm) and $\rho$ the density of the fluid.

Since the pixel values are linearly proportional to the intensity of the light reaching the CCD sensor, the image can be thought of as a two dimensional mapping of the chordal average amount of liquid metal, along the beam path. If one assumes that the liquid vapour or the injected gas are void within the liquid metal, then the liquid metal chordal average can be related to the void fraction as:

$$\alpha(x,y) = 1 - \frac{z_{\text{liquid}}(x,y)}{z_0(x,y)} \quad (11.62)$$

in which $z_0(x,y)$ is the amount of liquid metal along the beam path for zero void at the individual test conditions. Running an arbitrary experiment at different temperatures the thermal expansions both of the liquid metal and the test sections has to be taken into account, since both quantities modify the density the X-ray beam faces.

The difficulty in the data reduction is in determining how to compensate for the scatter of X-rays. This is frequently neglected in studies with much thinner test sections and low energy X-rays. But our test section is several mean free paths thick, and therefore produces a significant amount of scatter when high energy X-rays are used. If the scattered X-rays are distributed homogeneously in the plane of the glass screen, the previously mentioned linear relationship between the chordal average amount of tin and the grey level is maintained and each individual image may be calibrated using two known
points to define the relationship between the grey level and liquid metal thickness. These two points allow the slope, \( m \), and intercept, \( b \), to be calculated and a calibration line may be defined as:

\[
P_{\text{liquid}}(x, y) = b - m \cdot z_{\text{liquid}}(x, y)
\]  

(11.63)

In order to check for this linear relationship a solid liquid metal piece is inserted into the test section and a large amount of images has to be taken. By an averaging procedure one single image is obtained. This procedure substantially reduces the noise in the image and is the preferred method of quantitative imaging of static objects. The mean grey level for the pixels in the image of each step can then be measured. Repeating this procedure with liquid metal pieces of different thickness a linear relation between grey level and liquid metal thickness should be obtained. If the secondary radiation is not as assumed above, the void distribution in the test section would effect the calibration. A series of performance experiments conducted by [Baker & Bonazza, 1996] in which the void fraction distribution within a test box was artificially changed by means of Styrofoam balls demonstrated that there is little to no effect on the measurement of void fraction due to void distribution.

Once established that a linear relationship between grey level and liquid metal chordal average thickness exists, the calibration of each individual image in an experimental run can be accomplished with two points to define the calibration line. The grey level associated with 0% void is determined from the darkest pixel value. Typically this region is in the bottom corners of the test section or between the two injection ports for gas lifting. Depending on the height of the liquid metal within the test section, the grey level associated with 100% void is determined from either the region above the level of the liquid surface; or from the image of a hollow steel tube, sealed at both ends, of the same chordal length as the test section, placed at the upper right corner of the field of view. The linear relationship between these two points is used to relate the spectrum of grey levels to the chordal average amount of the liquid metal. An example of a two dimensional map of void fraction is shown in Figure 11.5.2(b) for an experiment that involved only gas injection into 11 kg of molten tin by [Bonazza & Baker, 1998]. There, twelve grey levels in the image represent equal bands of void fraction between 0% and 100%. For example, the darkest grey level represents a void fraction band of 0-8.3% void while the next grey level represents 8.4-16.6% void and so on. The integral (volume averaged) void fraction for the image can be obtained by calculating an average grey level weighted by the number of pixels in each band in the image, \( N_i \), as follows:

\[
\alpha = \frac{\sum_i N_i \alpha_i}{\sum_i N_i}
\]  

(11.64)

where \( \alpha \) represents the average void fraction for the \( i \)-th band with \( N_i \) pixels. The conditions exhibited in Figure 11.5.2(b) represent an average void fraction of 25.9% for the entire volume.

**Noise and unsharpness**

Although image quality is frequently discussed on the basis of sharpness and contrast, these are poor measures for a quantitative analysis of the errors involved in void fraction measurement. As suggested by [Macovski, 1983], a better measure is the signal-to-noise ratio (SNR) defined as:

\[
\text{SNR} = \frac{(I_2 - I_1)}{SD}
\]  

(11.65)

where \( I_1 \) is the background or 100% void signal, \( I_2 \) is the signal of interest, and SD is the standard deviation of \( I_2 \). The processes that must be considered to estimate the signal-to-noise ratio are photon
generation, photon interaction with the test section and metal, photon to light conversion in the glass screen, light collection through two lenses, the light photon conversion to electrons in the image intensifier and the CCD sensor, and the signal digitisation. If one assumes that the energy of the X-ray source is either constant or Poisson distributed, then the photons that are emitted from the source are Poisson distributed with parameter $N$, the number of photons emitted. The transmission of the beam through the test section is accounted for by modelling the beam absorption in the structural steel and liquid metal as a series of binomial processes. The beam that exits the test section is therefore still Poisson distributed, but with parameter $M$ given by:

$$
M = N \cdot \exp \left[ -\left( \frac{\mu_{\text{steel}}}{\rho_{\text{steel}}} \right) z_{\text{steel}} \right] \exp \left[ -\left( \frac{\mu_{\text{metal}}}{\rho_{\text{metal}}} \right) z_{\text{metal}} \right]
$$

(11.66)

assuming the test section to be made of steel and the subscript “metal” indicating the liquid metal to be investigated. As for any Poisson distributed random variable with parameter $M$, the standard deviation is just the square root of $M$.

To account for the glass screen, intensifier and camera, several processes must be included. First, the screen must absorb or interact with an incoming photon. This process may also be modelled as a binomial process. Second, the production of light photons following X-ray absorption is modelled as a Poisson process. Then, the intensifier and CCD camera are modelled as additional Poisson distributed amplification stages that account for photon to electron and electron to photon conversions in the intensifier as well as the light collection efficiency of the camera. As derived by several authors, including [Macovski, 1983], this results in the following expression for SNR:

$$
\text{SNR} = \left( \frac{I_s - I_x}{I_s} \right) \cdot \frac{\exp \left[ -\mu_{x_s} x_s \right] M}{\sqrt{1 + \frac{1}{g_1} + \frac{1}{g_1 g_2} + \frac{1}{g_1 g_2 g_3}}}
$$

(11.67)

where $g_1$, $g_2$, and $g_3$ are the gains of the glass screen, image intensifier and camera respectively.

The last step in the imaging chain is the digitisation that occurs in the CCD camera. This increases the noise in the image by the factor $F_D$, derived by [Swin nell, et al., 1991]:

$$
F_D = \left[ 1 + \frac{1}{12} \left( \frac{N_m \cdot \text{SD}}{2^8} \right) \right]^{\frac{1}{2}}
$$

(11.68)

where $N_m$ is the number of electrons required to produce a maximum video signal and SD is the standard deviation of the signal prior to digitisation. The final factor which must be accounted for is the effect of X-ray scatter on the SNR. Scatter produces an additive noise to that of the primary photons already accounted for. The scatter reduces the SNR by a factor $F_s$, which depends on the number of photons in the primary beam, $N_p$, the number of photons at the imaging plane due to scatter, $N_s$, and the ratio, $q$, of the glass screen X-ray to light conversion efficiencies for scatter and primary photons. $F_s$ was shown by [Jaffray, et al., 1994] to be:

$$
F_s = \frac{1}{\sqrt{1 + \left( q \cdot \frac{N_s}{N_p} \right)}}
$$

(11.69)
Scattered photons are at a lower energy than the primary photons so they have a lower absorption probability but a higher light production per absorbed photon. Using the correction for the parameters discussed, one can estimate the maximum error in the void fraction determination.

To illustrate the effect of noise, one can determine the minimum size void that would be detectable in a liquid metal pool. A common method to determine the size of a void that is detectable by a human observer is to assume that contrast must be at least five times the noise in the system. The void detectability and image quality are also limited by the image unsharpness which can be attributed to three sources. First, the finite size of the X-ray source focal spot creates a geometric distortion or penumbra. Second, the inherent characteristics of the glass screen limit resolution as does the requirement that the size of an area imaged by a single pixel of the camera must be at least a half of the detectable void size. Overall, it is evident that noise considerations will limit void detectability to a much larger extent than the image unsharpness produced in the digital imaging system.

**Errors due to mixture dynamics**

In addition to the effects of system noise, scatter, and image unsharpness on the visualisation and measurement of void fraction, the effects of the multiphase system dynamics on the measurement accuracy must be analysed. The most significant source of error is the motion of the liquid metal and gases and the consequent void fraction fluctuations during the time required to obtain an image. The fluctuations in the amount of void along the beam path increase the transmission of X-rays through the mixture as shown by [Harms & Laratta, 1973] and [Oyedele & Akintola, 1991]. Examples of phenomena that could result in these fluctuations are bubble growth or movement in the test section as shown in Figure 11.5.3. This effect will result in the present measurements overestimating the actual void fraction. If one models the void fluctuations as variations about a mean, \( \alpha + \Delta \alpha \), then the transmittance of X-rays is increased by a factor \( F_T \), derived by:

\[
F_T = 1 + \frac{\lambda^2 (\Delta \alpha)^2}{2}, \quad \Delta \alpha = \frac{1}{\lambda} \ln \left[ \frac{1}{\tau (m)} \exp(\lambda \alpha(t)) dt \right] - \frac{1}{\tau (m)} \int \alpha(t) dt
\]

where \( \lambda \) is the number of mean free paths along the beam direction through the test section. An expression for this dynamic error was subsequently derived by [Harms & Laratta, 1973] as Eq. (11.70)b.

In this equation \( t \) is the time required to collect one image frame. A detailed knowledge of the void fluctuation with time is required to estimate the error. Since this information is mostly not available, reasonable estimates of the largest possible fluctuations must be made from the rise velocity of bubbles in the multiphase mixture.

**Figure 11.5.3. Illustration of the void dynamics that increase X-ray transmission.** Void growth or the increase in the number of voids along the beam path as illustrated in Case 1 will increase transmission. Void movement or change in distribution without a change in the total void along the beam path, as illustrated in Case 2 will not result in a transient change in X-ray transmission.
11.5.2.2 \( \gamma \)-ray absorption

Because of extreme complexity of two-phase flows, most of the well known empirical relations and models give area averaged void fractions. Since void fraction varies across the cross-section of the pipe, to determine averaged void fraction, void fraction profiles as a function of radial distance should be determined. This can be two-dimensionally through one cross-section determined by means of the \( \gamma \)-ray absorption technique.

Figure 11.5.4. Scheme for the cross-sectional measurement of the two-dimensional void fraction profile using \( \gamma \)-ray absorption from [Satyamurthy, et al., 1998]

For this purpose the cross-section of the two-phase-flow in the pipe is assumed to have a number of circular zones owing a uniform void fraction in each zone. This is schematically depicted in Figure 11.5.4. Consider now “\( m \)” circular zones having the void fractions \( \alpha_1, \alpha_2, \ldots, \alpha_m \) to be determined and additionally let \( \beta_1, \beta_2, \ldots, \beta_n \) be the measured void fractions at the various chord lengths, then one gets:

\[
\beta_i = \sum_{j=1}^{m} \frac{d_{ij}}{c_i} \alpha_j \tag{11.71}
\]

where \( c_i \) is the total path length for the gamma ray at the \( i \)-th chord length and \( d_{ij} \) is the length of the \( j \)-th zone intercepted by the gamma ray beam at the \( i \)-th chord length. \( \beta_i \) are obtained from measured gamma ray intensities at the \( i \)-th chord with gas alone \( (I_{i,g}) \), with liquid metal alone \( (I_{i,l}) \) and when two-phase flow is present \( (I_{i,t}) \) and are given by:

\[
\beta_i = \ln \begin{bmatrix} I_{i,t} \\ I_{i,l} \\ I_{i,g} \end{bmatrix} \tag{11.72}
\]
Let $E$ be the error function defined as follows:

$$E^2 = \left( \sum_{i=1}^{n} \beta_i - \sum_{i=1}^{n} \frac{d_i}{\epsilon_i} \alpha \right)^2$$  \hspace{1cm} (11.73)

The minimisation of $E$ with respect to the $m$ parameters of $\alpha_1, \alpha_2, \ldots, \alpha_m$ gives a set of of $m$ linear equations. Using the measured values of $\beta_1, \beta_2, \ldots, \beta_n$, the values of $\alpha$ are obtained.

In the experiment performed by [Satyamurthy, et al., 1998] in a mercury nitrogen mixture, the number of chords chosen was 38 with 2.0 mm spacing. Seven zones were assumed. From the void fraction profiles, the area averaged void fraction was determined. The beam diameter (3 mm) was chosen so that finite beam errors were negligible [Satyamurthy, et al., 1994] besides obtaining a large number of zones. Number of counts were taken in excess of 6000 for every measurement so that statistical scalations were negligible (<1.5%) [Munshi & Vaidya, 1993]. In addition, dynamic void fluctuation corrections were estimated to determine the error range in the analysis [Thiyagarajan, et al., 1991].

**Corrections for the void-fraction measurements**

In a two-phase flow, void fraction fluctuation increases the radiation transmittance. Because of this the measured void fraction from this transmitted radiation intensity will be greater than the time-averaged void fraction [Harms & Forrest, 1971]. The effect of these fluctuations with respect to the attenuation parameter $\lambda = \mu/\rho$ is studied in detail by [Thiyagarajan, et al., 1991]. If the fluctuation magnitude (maximum deviation from average) is known, then the exact error due to the fluctuation can be determined. Corrections for two types of fluctuations – large ones (±100% deviation from the average) and medium ones (±50% deviation from the average) – have been worked out for a given attenuation parameter. Due to the non-availability of data on the degree of fluctuation in the experiment, the required correction for dynamic fluctuation is applied by the following procedure. The fluctuation correction for maximum possible fluctuation magnitude (±100% deviation from average) is applied to the measured data $\beta'$, and the corrected value $\beta''$ is obtained. The exact dynamic fluctuation-corrected void fraction lies between $\beta'$ and $\beta''$. Radial void fraction profiles are obtained separately with the uncorrected data ($\beta'$) and the corrected data ($\beta''$). The average of the two profiles is considered the dynamic fluctuation-corrected void fraction profile.

**Statistical fluctuation correction**

Radioactive decay obeys Poisson’s distribution law and is prone to random statistical fluctuations in the gamma-ray emission. It is well known from counting statistics that the maximum error involved in any intensity counts $N$ is equal to $N^{1/2}$. Since the measured void fraction is related to three intensities as given in Eq. (11.73), the effect of statistical fluctuation has to be determined. In this method, it can be shown that the error due to statistical fluctuation is described by Eq. (11.74).

$$\frac{\Delta \alpha}{\alpha} = \frac{1}{\alpha} \left( \frac{1}{\ln(I_g/I_i)} \right) \left[ \frac{1}{I} + \frac{\alpha^2}{I_g} + \frac{(\alpha-1)^2}{I_i} \right]^{1/2}$$  \hspace{1cm} (11.74)

Herein, $\epsilon_i$ is the dimensionless error in one particular measurement.

**Calibration, effort and accuracy**

Due to the high density especially of the heavy liquid metals quite strong $\gamma$-sources are required. In case of [Satyamurthy, et al., 1998] a cobalt-60 emitter with an activity of 2775 MBq was chosen as
the γ-ray source. Moreover, for the measurements 1.33 MeV photons were used which expands the capabilities of most of the liquid metal laboratories.

To determine the overall accuracy in measuring the void fraction profile, a static simulation system of gas and liquid metal is required similarly as for the X-ray technique in order to determine the individual levels corresponding to a specific void fraction value. The output of this process which must be performed with the liquids later used in the experiment is a calibration curve. If this is properly done void fraction profiles with an accuracy of about ±5% can be measured with the γ-ray absorption.

11.5.2.3 Neutron radiography (NR)

Neutron radiography (NR) is one of radiographic techniques which make use of the difference in attenuation characteristics of neutrons in materials [von der Hardt and Röttger, 1981]. Since thermal neutrons easily penetrate heavy materials like dense metals and are attenuated well by light materials as those containing hydrogen, NR was developed as a technique for non-destructive inspection which is complementary to X-ray radiography in the automobile and aerospace industries [Barton, 1993]. Recently, the application has spread to various scientific fields such as agricultural, medical and dental sciences, as well as application to porous materials like concrete and brick. Moreover, fluid research with use of the dynamic method of NR, namely the real-time NR has been a great hit because this technique is suitable for visualisation of a multiphase flow in a metallic casing [Mishima, et al., 1992; Hibiki, et al., 1994a] and a liquid metal [Takenaka, et al., 1994]. With spreading application fields, it is thought that the research trend is changing from qualitative to quantitative applications. Some attempts have been made to use NR not only as a tool for visualisation but also as a tool for quantitative measurement. Quantitative utilisation can be classified into two categories.

The first is to use the geometrical information extracted from NR images, for example, a measurement of particle trajectory and velocity [Ogino, et al., 1994], and hold up in a fluidised bed [Chiba, et al., 1989]. The second is to use the attenuation characteristics of neutrons in materials, for instance, measurement of void fraction in multiphase flow [Mishima, et al., 1993], [Hibiki, et al., 1993]. For this purpose, quantification method, namely the Σ-scaling method was developed [Hibiki & Mishima, 1996].

Basic concept of the neutron radiography

The mass attenuation coefficient of X-rays increases monotonically with the atomic number. On the other hand, thermal neutrons easily penetrate most of metals, while they are attenuated well by such materials as hydrogen, water, boron, gadolinium and cadmium. In other words, X-ray radiography takes advantage of the difference in densities, while NR takes advantage of the difference in neutron absorption cross-sections. Therefore, it is clear that NR is more suitable for observing the fluid behaviour in a metallic duct and liquid metals.

The block diagram of the imaging system for high-frame-rate NR with a steady neutron beam is shown in Figure 11.5.5. Here, the test section is set up in front (right-hand side) of the scintillator. When the neutron beam penetrates two-phase flow in the test section, the beam is attenuated in proportion to the liquid layer thickness along its path. Thus, the neutron beam projects the image of two-phase flow. The neutron beam which conveys the image of two-phase flow is changed into an optical image by the scintillator. The luminous intensity of the optical image is then increased by an image intensifier to obtain a better image. After the image is enlarged with a telephotographic lens, it
Figure 11.5.5. Schematic view of the neutron components falling on the converter screen and the subsequent path for processing the data for the void fraction measurement using neutron radiography (NR)

\[
\begin{align*}
\frac{1}{c_{73}} & = \frac{1}{c_{73}} + \frac{1}{c_{73}} + \frac{1}{c_{73}} + \frac{1}{c_{73}} + \frac{1}{c_{73}} + \frac{1}{c_{73}} + \frac{1}{c_{73}} \\
\phi_0 & = \phi_0 + \phi_m \\
n & = n + n + n + n + n + n + n + n + n + n
\end{align*}
\]

is detected with a high-speed video camera. The quality of the obtained image can be improved by using an image processing system consisted of an image memory and image processor. The following are necessary conditions to achieve a high-frame-rate NR for liquid metal two-phase flows:

a) a considerable large high flux neutron source (nuclear reactor);

b) a high sensitivity scintillator;

c) a high-speed video system with high reliability and long recording time;

d) a high performance image intensifier or a high sensitivity camera.

Each condition is discussed briefly below.

a) The neutron source

The neutron beam of thermal reactors is not mono-energetic. The spectrum has a Maxwellian distribution in the thermal region, a distribution proportional to \(1/E\) above 0.5 eV, and a bump in the fast region around 2 MeV. Above 10 MeV, the distribution drops rapidly. In sample materials this leads to beam hardening. As the sample becomes thicker, the lower energy parts of the spectrum are depleted at a faster rate than the higher energy parts because of the larger cross-section at low energy, decreasing the effective attenuation coefficient for thicker samples. Thus, a correction for beam hardening is inevitable.
Fast neutron radiography (FNR) is attractive as a non-destructive inspection technique due to the excellent matter penetration characteristics of fast neutrons. It is especially suitable for non-destructive inspection of industrial products that are too thick or dense to be inspected by conventional thermal neutron radiography (NR). Despite the availability of various fast neutron sources such as nuclear reactors, radioisotopes, and accelerators without a neutron moderator, FNR is not in widespread use. One of the reasons for this is the difficulties in clearly discriminating γ-rays associated with the neutron beam. These problems were overcome by the use of imaging plates with γ-ray discrimination [Matsubayashi, et al., 2001] and an FNR converter using wavelength-shifting fibres [Matsubayashi, et al., 2003].

b) Conversion screen or scintillator

The scintillator to be used in high-frame-rate NR should have characteristics of a high light yield, high resolution, short light decay time. Since rare earth scintillators of gadolinium compounds have a long light-decay time and glass scintillators have a low light-yield, these are not applicable to high-frame-rate NR. Only zinc sulphide scintillators mixed with lithium fluoride meets currently the above three conditions.

c) High speed camera

The purpose of developing high-frame-rate NR with a steady neutron beam is to visualise rapid phenomena for a long time period. Therefore, a high-speed video with a long recording time should be used, although the sensitivity is also important.

d) Image intensifier

Regarding the image intensifier a high amplification rate of order 105 with a high frame rate and a high resolution in terms of ‘line pairs per millimetres is required to capture oscillations. The image intensifier has to be matched to the high speed camera.

Due to the oscillations of the neutron spectrum in a reactor, spatial variations of the beam and varying random noise a lot of effort has to be spent in the pre-processing of images to correct systematic noise errors. A detailed description of this procedure can be found in [Richards, et al., 2004]. Once the pre-processing is done and the reference measurements to obtain the flat field images for a single-phase only (gas/liquid), no duct inside are conducted in order to correct for scattering, etc. the void fraction measurement can start.

The principle of the void fraction measurement

The flux of incident neutron \( \phi_{th} \) is attenuated in the liquid and the structure material of the test section, thus:

\[
\phi = \phi_{th} \cdot \exp \left[ -\Sigma_a \delta_G - \Sigma_L \delta_{ML} - \Sigma_L \delta_L \right] + \phi_s
\]

where \( \phi \) and \( \phi_s \) denote the total neutron flux falling on the converter and scattered neutron component, respectively. Ignoring the neutron absorption in the gas phase, the measured grey levels \( G \) are given by the following equations for the gas-filled (subscript “G”), liquid-filled (subscript “L”), and two-phase mixture-filled (subscript “ML”) test sections.
where \( G_0 \) is the offset term which consists of scattered neutron component \( G_S \) and dark current \( G_D \);
\[
G_0 = G_S + G_D.
\]
The tilde (\( \sim \)) denotes that the grey levels among the images were normalised, i.e. by matching the reference brightness at some point outside the test section where neutron attenuation is negligible. Usually the dark current term \( G_D \) is uniform and can be treated as an offset. On the other hand the scattered neutron component \( G_S \) is not always uniform. To treat \( G_0 \) as an offset, the scattered neutron component \( G_S \) should be spatially uniform. The scattered neutron component \( G_S \) consists of neutrons scattered in the test section \( G_{SM} \) and those scattered in the surrounding background objects \( G_{SS} \):
\[
G_S = G_{SM} + G_{SS} = C(\phi_{SM} + \phi_{SS})
\]
Since \( \phi_{SS} \) is, in most cases, spatially uniform, the scattered neutron component \( G_S \) could be made spatially uniform if \( \phi_{SM} \) is spatially uniform or negligible. This condition can be achieved by taking a sufficiently large distance \( L' \) between the test section and the converter. The minimum of this distance is currently being estimated experimentally to be about the width of the test section. With this uniform \( G_S \), the term \( G_0 \) can be treated as a constant offset. Then, from Eq. (11.76), the offset term \( G_0 \) can be determined using the grey levels obtained from the liquid filled and gas-filled test sections by:
\[
G_0 = G_S + G_D = \frac{G_L^0 - C \phi_{in} \exp\left[-\Sigma, \delta_L\right] + G_0}{1 - \exp\left[-\Sigma, \delta_L\right]}
\]
Finally, the void fraction \( \alpha \) is obtained by:
\[
\alpha_0 = 1 - \frac{\delta_{ML}}{\delta_L} = \frac{\ln\left(G_L / G_M\right)}{\ln\left(G_L / G_G\right)} = \frac{\ln\left(G_L^0 - G_0 / G_M^0 - G_0\right)}{\ln\left(G_L^0 - G_0 / G_G^0 - G_0\right)}
\]
In this method, the offset term \( G_0 \) is determined based upon the total macroscopic cross-section \( \Sigma_L \), and quantitative information is derived from grey levels which are relative quantities by nature. In this sense, this is called \( \Sigma \)-scaling method. As discussed above, this method assumes that the offset term \( G_0 \) can be made spatially uniform by taking a large distance \( L' \). It should be noted here that the un-parallelness of the incident neutron beam causes image blur, especially in the vicinity of material boundary. The spatial resolution is given by the distance \( L' \) and the \( L/D \) ratio of the NR facilities as follows:
\[
R = \frac{L'}{(L/D)}
\]
Therefore the appropriate range of \( L' \) to be used in f-scaling method should be an optimum value taking account of the above two requirements. This method was tested with a known void profile [Matsubayashi, et al., 2004].

Moreover, to confirm this method for the void fraction of two-phase flow in a rectangular duct gas velocities calculated from the void fractions measured by the NR method are compared with those by conductance probe methods [Mishima, et al., 1993], [Saito, et al., 2005] as shown in Figure 11.5.6(a). Since the measured values by high-frame-rate NR are particularly affected by the statistical variation
of neutrons, the integrated image of the images obtained by the real-time NR with the recording speed of 30 frames per second instead of the high-frame-rate NR was used here. The solid line indicates the prediction by the drift flux correlation for a rectangular duct [Griffith, 1963], [Ishii, 1977]. It is shown that the measured values are consistent with each other and correlated well by the drift flux correlation. The measurement error by the NR method is estimated to be less than 5%. The sensitivity of the high speed NR compared to intrusive methods like resistive (or conductance) probes is by orders of magnitudes larger than the latter. They are not affected by local effects close to a probe tip, wetting effects are material compatibility. With one scan consisting of several frames a complete void fraction profile along a tube can be acquired. By using an Abel integration, which implicitly assumes axis-symmetry even the two-dimensional void fraction profiles can be reconstructed, see [Saito, et al., 2004, 2005]. A comparison of the NR performance and its resolution to a conductance probe is shown in Figure 11.5.6(b) on the example of a time series of the measured void fraction.

11.5.3 Resistive or conductance probes

The resistive probes are local sensors with an electrically conducting tip (Cr/Ni wires, tungsten, stainless steel or platinum, with diameters \( \geq 0.1 \) mm) in direct contact with the liquid. These kinds of probes are usually supplied with an AC current operating typically at frequencies in the range from 1-25 kHz. The AC source induces an electric current flowing from the probe tip to an opposite electrode (e.g. the probe support or the channel wall). The gas contact at the sensitive wire is detected by an interrupt of the electrical current. Due to the huge differences in the electrical conductivity between the gas and the metal, one obtains sharp signals easy to evaluate by a threshold method.

The measuring quantity is the ratio of the gas contact time to the total sampling time. This ratio yields a time averaged local void fraction. From this method also the number of bubbles during the total sampling time are known and hence the bubble frequency. The measurement principle of resistive probes is shown in Figure 11.5.7.
If the probe is supplied with a single wire tip the local void fraction $\alpha$ can be measured. A double wire probe, where the two electrodes are installed with a distinct displacement in flow direction, allows in addition the determination of the bubble velocity from the time delay of the signal between both electrodes. Further, the bubble chords can be yielded from the product of the velocity and the measured gas contact time at the probe. Methods to transform the chord-length distributions into bubble-size distributions have been suggested by several authors. In any case the significant interaction between the bubbles and the local sensor has to be taken into account. Large measuring errors have to be expected for the measurement of the bubble velocity or the chord length by means of double-wire probes if not appropriate measures are taken.

The electrical resistive probe method is attractive for bubbly flow measurements because of its relative simplicity and wide applicability. It detects the passage of interfaces at the tip of each sensor, and uses this data to determine void fraction and bubble size and velocity, see [Delhaye, 1983], [Serizawa, et al., 1975] or [Kocamustafaogullari & Wang, 1991]. The optic fibre has a faster response, but besides the opaqueness of liquid metals, the found commercial probes are both expensive and too fragile to use in heavy liquid metals and in the large bubble column experiments typically appearing.

Early versions involved only one needle, which gave two different signals depending upon whether the needle tip was in a bubble or in liquid. [Hills, 1974] used a short needle with a single 90° bend and investigated the radial variation of gas hold-up in a vertical bubble column. [Neal and Bankoff, 1963] also used the single 90° bend configuration and analysed bubble signals in terms of autocorrelation functions to obtain local values of gas fraction, bubble frequencies and bubble size.

[Serizawa, et al., 1975] developed the method further and presented a double-sensor probe for measuring local values of air-water bubbly flows. This probe had the advantage that it was capable of measuring bubble velocity from the time lag between a pair of upstream-downstream signals. It consisted of two identical electrically insulated needles placed side-by-side with their tips about 5.0 mm apart. [Kocamustafagullari & Wang, 1991] recommended a 2.5 mm separation to account for possible bubble size and bubble velocity. A comprehensive list of previous probe designs is given in [Sanaullah, et al., 2001]. The problem with the two-point probe is the difficulty of matching the signals from the two needles which correspond to the same bubble, especially since bubbles do not always rise vertically, and often strike the probe with a glancing blow.
One attempt to improve the situation is to use a five-point probe [Burgess & Calderbank, 1975] or [Buchholz & Steinemann, 1984] with a leading needle surrounded by four needle tips in the same horizontal plane a few millimetres downstream of the central tip. The extra complexity involved has meant that these devices have not been used as much as the simpler two-point probe. One of the major concerns with multiple probes is that the leading needle may interfere with the bubble, and so disturb the reading of the downstream needle(s). The Burgess & Calderbank’s algorithm (1975) for analysing data from his five-point probe rejected any bubble not seen simultaneously by three equi-spaced downstream needles, thus ensuring that only “head-on” collisions, least likely to be affected, were analysed. This, however, meant that only a very small sample of the bubble population was included, raising doubts about whether the sample was representative.

The orientation of the resistive probe needles is commonly either horizontal (perpendicular to the bubble path) or vertical. In the horizontal configuration, the ability of the probe to withstand the lateral drag of the fluid becomes an important factor; in the double needle probe, this leads to uncertainty about the exact vertical positions, and hence the separation, of the tips. However, with any double sensor probe, the two tips must be vertically one above the other, which is impossible if both needles are vertical. Most recent workers have used two very fine needles touching each other. However, the use of touching needles means that there is a danger of the liquid meniscus in the channel between them affecting the behaviour of the downstream needle tip. A common orientation in commercial two-point optic-fibre probes is to separate the two needles, but to bend the upstream one so that the two tips are aligned, but this raises the question as to whether the different orientations of the two probes influences the result.

**Probe design**

A design of a two-pole and a four pole probe used in liquid metal experiments is shown in the Figures 11.5.8. The wires have usually a distance of 2-5 mm from each other and are aligned with respect to the main flow direction. A too large a separation can introduce errors in the detected signals as multi-bubble contact may occur between two signals originating from the same bubble, whereas too small a separation will lead to errors in the estimation of velocity. The two sensors are electrically insulated from the probe body, except their tips, which are made by simply cutting the ends off the insulated wires. The other ends of the wires are soldered to two coaxial cables. The soldered connections are carefully electrically insulated using air dried insulating varnish and as an additional measure for safe insulation soldered connections are wrapped by heat shrinking plastic tubes. The other

**Figure 11.5.8.** (a) Schematic illustration of an inclined dual-sensor resistive probe from [Sanaulla, *et al.*, 2001]. (b) Sketch of a four-pole resistive sensor used in PbBi by [Saito, *et al.*, 2005].

![Diagram of probe design](image)
ends of the coaxial cables are connected to the bubble signal processor. The screens of these cables are joined to a lead whose other end touches the liquid metal in the column as the “ground”. The signal processor mainly compares the resistance between the probe tip and the ground. A constant potential of several volts DC is applied across each needle and the potential across a series resistor is amplified to provide the output signal.

Data processing

The raw signals obtained by the probe are not square-waves as to ideal contact or not. This is due to the relatively slow drainage of liquid film formed around the sensor tip, which leads to a slow rise time as compared to the sharp fall time when the sensor re-enters the water. To obtain bubble properties, it is necessary to have data in terms of perfect square-waves with the rise and fall corresponding to the precise moment when the needle enters and leaves the gas phase. For this purpose, the raw data are differentiated, and the moment when the value of the derivative crosses a certain threshold is used as the interface contact time. This processing can be implemented via software algorithms. A detailed description is given in the thesis of [Cheng, 1997].

The local void fraction $\alpha$ can be calculated from the sum of duration time $t_g$ for bubbles at the upstream probe for the sample time $T$:

$$\alpha = \frac{\sum t_g}{T}. \quad (11.81)$$

Using the time lag between the signals for the two sensors and the vertical distance $L$ between them, the velocity of the $i$-th bubble, $u_{Bi}$, can be determined by:

$$u_{Bi} = \frac{L}{t_{di}} \quad (11.82)$$

where the average displacement time of liquid-gas interface and gas-liquid interface for a bubble travelling between the two sensors is given as:

$$t_{di} = \frac{1}{2}(t_{di} - t_{ui}) + \frac{1}{2}(t_{gi} - t_{df}) \quad (11.83)$$

where subscript “$d$” and “$u$” corresponds to downstream and upstream, respectively, and “$r$” and “$f$” corresponds to rise and fall signals, respectively. The bubble chord length $L_{Bi}$ is then obtained as:

$$L_{Bi} = u_{Bi}(t_{ui} - t_{df}) \quad (11.84)$$

where the upstream contact time is used, as explained above, for its greater reliability.

Estimating bubble size distribution from the bubble chord length distribution is not easy, and even estimating the mean bubble size and velocity is not without problems. Since the probe is more likely to see a large bubble than a small one, complicated weighting factors are needed. In order to use the resistive probe for two-phase studies, it is most important to establish a statistical model that relates the local interfacial area concentration to the measured quantities. Over the past twenty years, different statistical models for local interfacial area concentration measurement using a double-sensor probe have been developed. In this context only the four most common models are described. The evaluation of multi-tip probes is more sophisticated and requires several estimates, which would expand the scope.
of this presentation. A detailed description of the methods there required is given in the papers by [Dias, et al., 2000], [Kim, et al., 2001] or [Shen, et al., 2005]. Here, only the different methods for two-tip arrangements are described.

**Statistical methods to evaluate the local interfacial area concentration**

a) Kataoka’s statistical model (1986)

According to the definition of the local interfacial area concentration by [Ishii, 1975], [Kataoka, et al., 1986] carried out derivations and established a statistical model that related the local time-averaged interfacial area concentration \(a_i\) to the harmonic mean of the interfacial velocity. Consider the main flow is in \(z\)-direction. Assume that the bubbles are spherical, the probe passes every part of the bubbles with an equal probability, and there is no statistical relation between interfacial velocity and the angle between the interfacial velocity and the normal vector of the interface. With this statistical model the time-averaged interfacial area concentration can be expressed as:

\[
\bar{a}_i = 4N_i \frac{1}{u_{z ij}} \left( \frac{1}{1 - \cot \left( \frac{\alpha_0}{2} \right)} \ln \left( \frac{\cos \left( \frac{\alpha_0}{2} \right)}{2} \right) - \tan \left( \frac{\alpha_0}{2} \right) \ln \left( \frac{\sin \left( \frac{\alpha_0}{2} \right)}{2} \right) \right)
\]

(11.85)

where \(u_{z ij}, \alpha_0\) and \(N_i\) denote \(z\) component of the interfacial velocity, the maximum angle between the interfacial velocity and the mean flow direction, and the number of bubbles measured per unit time, respectively. On the derivation of Eq. (11.85), it is also assumed that the angle between the bubble interfacial velocity and the main flow direction, \(\alpha\), is random with an equal probability within some maximum angle \(\alpha_0\). The value of \(\alpha_0\) is determined from the statistical parameters of the measured interfacial velocity. Assuming that the interfacial velocity fluctuations in three directions are equilateral [Kataoka, et al., 1986] derived the relationship between the maximum angle \(\alpha_0\) and the standard deviation of bubble velocity fluctuation in the main flow direction with the following form:

\[
\frac{\sin 2\alpha_0}{2\alpha_0} = -\frac{1 - \sigma_i^2 / u_{z ij}^2}{1 + 3\sigma_i^2 / u_{z ij}^2}
\]

(11.86)

where \(\sigma_i\) denotes the root mean square of the interface velocity fluctuation. For more details on the mathematical modelling of this measurement method, one can refer to [Kataoka, et al., 1986]. The interfacial area \(a_i\) can then be used to estimate the Sauter mean diameter \(d_s\) using:

\[
d_s = \frac{6\bar{a}_i}{a_i}
\]

(11.87)

b) Kalkach-Navarro’s statistical model (1993)

[Kalkach-Navarro, et al., 1993] assumed that the bubbles were spherical and the bubble sizes were represented by a probability distribution function, \(f(V_j)\), where \(f(V_j)\) was the number of bubbles per unit volume having a volume between \(V_j\) and \(V_j + dV\). From the geometrical consideration, they proposed the following statistical model for local interfacial area concentration measurement:

\[
\bar{a}_i = \frac{36\pi}{5} \sum_j f(V_j) V_j^{2/3} dV_j
\]

(11.88)
where $V_j$ is the volume of the group-$j$ bubbles and calculated from the chord length measured by a double-sensor probe. In order to determine $f(V_j)$, the maximum chord length measured is divided into equal partitions, then a probability of each partition of chord length is obtained. Assuming the bubbles can be penetrated at any point with equal probability by the sensor tips, a triangular matrix, which represents the relationship between the probability of the chord length cut by sensors and the probability of bubble radius, is established. Then, the bubble size probability distribution function, $f(V_j)$, can be derived from the probability distribution of the bubble radius. In this model, however, the authors derive straightway the relations for local measurement from the chord length distributions, and take no account for the effect of bubble lateral motions.

c) Hibiki’s statistical model (1998)

[Hibiki, et al., 1998] conducted a similar derivation to Kataoka, et al. (1986) based on basically the same assumptions, except for the probability density function of $\alpha$, the angle between the bubble interfacial velocity and the main flow direction. In view that the probability density function of $\alpha$ has a peak in the main flow direction from the experimental data, they replaced the equal probability within a maximum angle of $\alpha_0$, using the following relations:

$$g(\alpha) = \begin{cases} 
\frac{1}{\alpha_0} (\alpha - \alpha_0)^2 & \text{for} \quad 0 \leq \alpha \leq \alpha_0 \\
0 & \text{for} \quad \alpha_0 \leq \alpha \leq \pi/2 
\end{cases}$$

(11.89)

They derived the following relations between the maximum angle, $\alpha_0$, and the standard deviation of bubble velocity fluctuation in the main flow direction:

$$\frac{3}{\alpha_0} \left(1 - \frac{\sin 2\alpha_0}{2\alpha_0}\right) = 1 - \frac{\sigma^2_{\alpha}}{u_{\alpha}^2} + 3\frac{\sigma^2_{\alpha}}{u_{\alpha}^2}$$

(11.90)

d) Wu’s statistical model (1999)

[Wu and Ishii, 1999] carried out sensitivity study through numerical method on double-sensor conductivity probe measuring local interfacial area concentration. They assume that the bubble velocity fluctuation is isotropic and the bubble is spherical. Considering the effects of bubble lateral motions and the distance between the two tips of the double-sensor probe, and taking the contribution of the missed bubbles into account, a statistical model is obtained also from the definition by [Ishii, 1975] as:

$$\bar{\alpha_i} = \frac{2N_b}{\Delta T(N_b - N_{\text{miss}})} \left[ \frac{1}{u_{\alpha}} \right] \left[ 2 + \left( \frac{\bar{u}_b}{u_b} \right)^{2.25} \right]$$

(11.91)

where $\Delta T, N_b, N_{\text{miss}}$, and $u_b/u_b$ denotes the sampling time, the total number of measured bubbles, the number of the missed bubbles, and relative bubble velocity fluctuation, respectively. The missed bubbles referred to those that are touched by the first sensor but not by the second sensor, or those that pass the second sensor ahead of the first sensor in view of the bubble lateral motions. The number of the missed bubbles can be obtained from the double-sensor probe signals directly. From numerical method, [Wu & Ishii, 1999] suggest the relative standard deviation of the inverse of the measured interfacial velocity to characterise the relative bubble velocity fluctuation with the following form:

$$\frac{\bar{u}_b}{u_b} = 0.85 \sqrt{1 + \frac{\sigma^2_{\alpha}}{u_{\alpha}^2}}$$

(11.92)
where 0.85 has been determined by their numerical analysis. When the bubble diameters are in the range from 1.2Δs to 3Δs, the authors report that the error of the above relation is in the range of ±10%, where Δs denoted the distance between the two tips of the double-sensor probe.

Experimental experience and accuracy

The impact of inclination of the probe with respect to the main flow is a critical issue. Here, especially the effect of the interaction between the two needles, by calculating bubble frequency or void fraction from the upstream or the downstream needle makes this obvious. The accuracy of the double tip probes can be checked by comparing the calculated values of the void fraction and the gas superficial velocities with those determined manometrically. The agreement is of course not better than the statistical methods used for the signal processing and thus around ±10%.

A better agreement is only obtained for more advanced statistical methods. If e.g. the bubbles are categorised into two groups, such that group one includes spherical and distorted bubbles and group two includes cap and slug bubbles, then correction methods in calculating the local \( a_i \) for missing and non-effective bubble signals can be formulated accounting for different contributions from various bubble interfaces. Such a procedure was successfully tested by [Kim, et al., 2001]. The deviation between experiment and numerical simulations shrinks to a few per cent only.

11.5.4 Ultrasound Doppler velocimetry (UDV) for two-phase flows

Detection of bubbles or particles in a dominant liquid two-phase flow inside pipes or vessels is important in research and industries. The ultrasonic pulse-echo method allows by means of liquid metal adapted waveguides to measure up to temperatures of 620°C [Eckert, et al., 2003], and dense media with a high sound velocity as gallium (~2600 m/s, compare [Brito, et al., 2001], however, to use the ultrasound technique for the determination of two-phase flows is quite new. A first attempt to analyse a two-phase flow using this technique was made by [Hofmann & Rockstroh, 1996]. There, a straight-beam transmitting-receiving probe transmits short bursts at regular intervals in the range 0.1 to 4 kHz and more, having an ultrasonic frequency in the range 1 to 10 MHz. The ultrasonic waves penetrate the wall and the two-phase flow. They will be directly reflected by the bubbles or particles and by the inner back wall of the vessel. The back wall echo is more intense in comparison with the direct echo in most cases. Reflected waves are received partially by the same probe and displayed on the screen of an ultrasonic echo detector as an echogram, as shown schematically in Figure 11.5.9(a).

If the sizes of objects (bubbles) and arrangements (structure elements like the pipe or an immersed body) are much greater than the ultrasonic wavelength the behaviour of ultrasonic waves can be considered as similar to optics in the following. If the inclination of reference object (the bubble) with respect to the emitter/sensor is too large, the cross-section the intensity of the received echo goes to zero. Assuming a homogeneous cylindrical sound field and neglecting any changes in wave mode, the largest inclination angle \( \alpha_{\theta0} \) of a plane reflector (bubble) to be allowed can be calculated as follows:

\[
\alpha_{\theta0} = \frac{1}{2} a \tan \left( \frac{d \Delta^\ell}{2c_s l_c \left( 1 + \frac{c_s l_c}{c_l l_f} \right)} \right)
\]

(11.93)

where \( c_s, c_l \) are the sound velocities of the wave guide and the liquid metal, \( l_c \) and \( l_f \) the length of the waveguide and the that of the fluid in sound direction, respectively. Having a probe transducer
diameter $d_p = 10$ mm, $l_t = 40$ mm, $l_s = 135$ mm, $c_l = 1730$ ms$^{-1}$ (liquid lead-bismuth), $c_s = 5730$ ms$^{-1}$ (stainless steel), this angle has a value of $\alpha_{g0} = 0.21^\circ$ only! That means, an echo cannot be received by the probe if $\alpha_R > 0.21^\circ$.

A great progress for the use of UDV in two-phase flows was achieved by the work of [Suzuki, et al., 2000, 2002]. When the ultrasound probe UVP is applied to bubbly flows, the system records velocities of both phases together. In their studies, the phase discrimination is made using pattern recognition. All stored instantaneous velocity profiles are classified into two groups with regard to existence of bubble data. If no bubble crosses the measuring line when an ultrasonic pulse is emitted, the obtained instantaneous velocity profile should give only negative values at all the measuring points in the channel. Such instantaneous velocity profiles are stored as Group A (ensemble averaged local liquid velocity profile distant from bubbles). On the other hand, if a bubble exists on the ultrasonic beam path, the obtained velocity profile has positive values near the gas-liquid interface. These profiles are stored as Group B (velocity profile around a bubble). The Group B profiles are rearranged according to the distance from the bubble’s surface. Furthermore, in relation to the influence of wakes behind leading bubbles, instantaneous velocity profiles of Group B are subdivided into two groups, Groups B1 and B2. Group B1 includes velocity profiles that contain effects of leading bubbles. When the instantaneous velocity profile is not affected by leading bubbles, the profile is categorised into Group B2. The presence of the wake effect is determined by another pattern recognition. If a positive small peak exists between the transducer and the bubble’s surface in an instantaneous velocity profile, that small peak is considered as the effect of the leading bubbles, or the wake. As a result of this pattern recognition and conditional sampling of data, the ensemble-averaged velocity is obtained at each relative distance from a bubble’s surface.

Eckert, et al. (2003) improved Suzuki’s technique and applied it to PbBi melts up to 300°C and CuSn melts with up to 620°C using nitrogen as gas. A sketch of their experimental set-up, which they referenced against a resistivity probe is shown in Figure 11.5.9(b).
An example of a typical velocity profile obtained from the bubbly flow can be seen in Figure 11.5.10(a). The lower velocity at the small measuring depths corresponds to the flow of the liquid metal that is driven by the rising bubbles. Since the ultrasonic pulse is reflected at the bubble interface, the velocity measured can be interpreted as an interfacial velocity. If the entire ultrasonic energy is reflected by the bubble as demonstrated in this example, no information can be received from measuring depths behind the bubble position, which is called the shadow effect. Measurements of the phase velocities and the bubble frequency can be obtained only for low void fractions ($\alpha < 0.1$), unless tomographic systems consisting of several transmitters and receivers are used as e.g. proposed by [Xu, et al., 1997] and [Beckord, et al., 1998]. However, such systems were currently not applied to liquid metal two-phase flows.

Figure 11.5.10. (a) Typical measured velocity profile of a single bubble case from [Eckert, et al., 2003]. (b) Example of a calculated probability density function to separate both phase velocities.

A phase separation of the measured velocities of the liquid and gas can be performed by calculating the corresponding probability density functions (PDFs). Here, the assumption is made that the PDFs of both phases can be expressed by a normal distribution, as shown for example in Figure 11.5.10(b). The PDFs were calculated in the [Eckert, et al., 2003] paper on the basis of 4.096 velocity profiles.

11.6 Temperature measurements

11.6.1 Thermocouples

The measurement of the liquid lead-bismuth temperature is usually performed using NiCr-Ni thermocouples being mantled by a stainless steel tubing. A careful determination of the temperature is necessary to determine the thermophysical data of the fluid. The diameter of the used elements varies between 0.25 mm and 3.0 mm depending on the time scales to be resolved at the desired location. Because of the high heat transfer coefficients that are characteristic of a liquid metal the frequency response of thermocouples is far higher than in conventional fluids. According to [Krebs & Bremhorst, 1983] a 0.25 mm sheathed thermocouple with an insulated junction gives undamped signals in sodium in excess of at maximum 40 Hz.

The temperature signal originating from a thermocouple arises from the thermo-electric effect. The connection of two different materials is called thermocouple. If two different types of metals are connected together by welding, soldering or only by twisting a voltage is generated. This can be
measured at the end of the two materials. At the connection of two different metals the electrons are changing from one metal into the other. Authoritatively for this process is the escape work of the electrons. The metal with the lower escape work delivers electrons and becomes positive. Thereby an electric field $\phi$ arises in the interface.

The contact voltage $\Delta\phi$ which is generated in the contact surface is proportional to the Boltzmann distribution of the temperature $T$ and also to the relation of the free-electron density $n_A$ and $n_B$. This is the so-called Seebeck effect.

$$
\Delta\phi = \frac{kT}{e_0} \ln \left( \frac{n_A}{n_B} \right)
$$

(11.94)

where $k$ is the Boltzmann constant and $e_0$ the elementary charge. The terms in the right side can be combined to the material constant $k_{AB}$. Then the equation reduces to:

$$
\Delta\phi = k_{AB} \cdot T
$$

(11.95)

About 13 “standard” thermocouple types are commonly used. Eight have been given internationally recognised letter type designators. The letter type designator refers to the electromotive force (emf) table, not the composition of the metals – so any thermocouple that matches the emf table within the defined tolerances may receive that table’s letter designator. Some of the non-recognised thermocouples may excel in particular niche applications and have gained a degree of acceptance for this reason, as well as due to effective marketing by the alloy manufacturer. Some of these have been given letter type designators by their manufacturers that have been partially accepted by industry. Each thermocouple type has characteristics that can be matched to applications. Industry generally prefers $K$ and $N$ types because of their suitability to high temperatures, while others often prefer the $T$ type due to its sensitivity, low cost and ease of use. In Table 11.6.1 the standard thermocouple types are presented. The table also shows the temperature range for extension grade wire in brackets.

There are four common ways in which thermocouples are mounted with in a stainless steel or Inconel sheath and electrically insulated with mineral oxides. Each of the methods has its advantages and disadvantages. Good relatively trouble-free arrangement will be reached by the sealed and isolated from sheath mounting. The principal reason for not using this arrangement for all applications is its sluggish response time – the typical time constant is 75 seconds. The sealed and grounded to sheath mounting can cause ground loops and other noise injection. But, it provides a reasonable time constant (40 seconds) and a sealed enclosure. A faster response time constant (typically 15 seconds) is given by the exposed bead mounting. But it lacks mechanical and chemical protection, and electrical isolation from material being measured. The porous insulating mineral oxides must be sealed.

The fastest response time constant is gotten by the exposed fast response type. Typically for this arrangement are 2 seconds but with fine gauge of junction wire the time constant can be 1-100 ms depending on their diameter. In addition to problems of the exposed bead type, the protruding and light construction makes the thermocouple more prone to physical damage.

Because of their physical characteristics, thermocouples are the preferred method of temperature measurement in many applications. They can be very rugged, are immune to shock and vibration, are useful over a wide temperature range, are simple to manufactured, require no excitation power, there is no self heating and they can be made very small. No other temperature sensor provides this degree of versatility. Thermocouples are wonderful sensors to experiment with because of their robustness, wide temperature range and unique properties.
Table 11.6.1. ANSI registered thermocouple groups containing the accuracy, range and composition

<table>
<thead>
<tr>
<th>Type</th>
<th>Positive material</th>
<th>Negative material</th>
<th>Accuracy*** Class 2</th>
<th>Range °C (extension)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>Pt, 30%Rh</td>
<td>Pt, 6%Rh</td>
<td>0.5% &gt;800°C</td>
<td>50 to 1820 (1 to 100)</td>
<td>Good at high temperatures, no reference junction compensation required.</td>
</tr>
<tr>
<td>C**</td>
<td>W, 5%Re</td>
<td>W, 26%Re</td>
<td>1% &gt;425°C</td>
<td>0 to 2315 (0 to 870)</td>
<td>Very high temperature use, brittle.</td>
</tr>
<tr>
<td>D**</td>
<td>W, 3%Re</td>
<td>W, 25%Re</td>
<td>1% &gt;425°C</td>
<td>0 to 2315 (0 to 260)</td>
<td>Very high temperature use, brittle.</td>
</tr>
<tr>
<td>E</td>
<td>Ni, 10%Cr</td>
<td>Cu, 45%Ni</td>
<td>0.5% or 1.7°C</td>
<td>-270 to 1000 (0 to 200)</td>
<td>General purpose, low and medium temperatures.</td>
</tr>
<tr>
<td>G**</td>
<td>W</td>
<td>W, 26%Re</td>
<td>1% &gt;425°C</td>
<td>0 to 2315 (0 to 260)</td>
<td>Very high temperature use, brittle.</td>
</tr>
<tr>
<td>J</td>
<td>Fe</td>
<td>Cu, 45%Ni</td>
<td>0.75% or 2.2°C</td>
<td>-210 to 1200 (0 to 200)</td>
<td>High temperature, reducing environment.</td>
</tr>
<tr>
<td>K*</td>
<td>Ni, 10%Cr</td>
<td>Ni, 2%Al 2%Mn 1%Si</td>
<td>0.75% or 2.2°C</td>
<td>-270 to 1372 (0 to 80)</td>
<td>General purpose high temperature, oxidising environment.</td>
</tr>
<tr>
<td>L**</td>
<td>Fe</td>
<td>Cu, 45%Ni</td>
<td>0.4% or 1.5°C</td>
<td>0 to 900</td>
<td>Similar to J type. Obsolete – not for new designs.</td>
</tr>
<tr>
<td>M**</td>
<td>Ni</td>
<td>Ni, 18%Mo</td>
<td>0.75% or 2.2°C</td>
<td>-50 to 1410</td>
<td></td>
</tr>
<tr>
<td>N*</td>
<td>Ni, 14%Cr 1.5%Si</td>
<td>Ni, 4.5%Si 0.1%Mg</td>
<td>0.75% or 2.2°C</td>
<td>-270 to 1300 (0 to 200)</td>
<td>Relatively new type as a superior replacement for K type.</td>
</tr>
<tr>
<td>P**</td>
<td>Platinel II</td>
<td>Platinel II</td>
<td>1.0%</td>
<td>0 to 1395</td>
<td>A more stable but expensive substitute for K &amp; N types.</td>
</tr>
<tr>
<td>R</td>
<td>Pt, 13%Rh</td>
<td>Pt</td>
<td>0.25% or 1.5°C</td>
<td>-50 to 1768 (0 to 50)</td>
<td>Precision, high temperature.</td>
</tr>
<tr>
<td>S</td>
<td>Pt, 10%Rh</td>
<td>Pt</td>
<td>0.25% or 1.5°C</td>
<td>-50 to 1768 (0 to 50)</td>
<td>Precision, high temperature.</td>
</tr>
<tr>
<td>T*</td>
<td>Cu</td>
<td>Cu, 45%Ni</td>
<td>0.75% or 1.0°C</td>
<td>-270 to 400 (-60 to 100)</td>
<td>Good general purpose, low temperature, tolerant to moisture.</td>
</tr>
<tr>
<td>U**</td>
<td>Cu</td>
<td>Cu, 45%Ni</td>
<td>0.4% or 1.5°C</td>
<td>0 to 600</td>
<td>Similar to T type. Obsolete – not for new designs.</td>
</tr>
</tbody>
</table>

* Most commonly used thermocouple types. ** Not ANSI recognised types. ***See IEC 584-2 for more details.


On the down side, the thermocouple produces a relative low output signal that is non-linear. These characteristics require a sensitive and stable measuring device that is able provide reference junction compensation and linearisation. Also the low signal level demands that a higher level of care be taken when installing to minimise potential noise sources. The measuring hardware requires good noise rejection capability. Ground loops can be a problem with non-isolated systems, unless the common mode range and rejection is adequate.

In case of monitoring the temperature in electromagnetic flow meters or electromagnetic pumps misreadings may occur due to the ferromagnetic properties of the Ni-NiCr thermocouple. This effect increases dramatically if temperature gradients or gradients of the magnetic field exist. Numerous effects listed afterwards can lead to misreadings and as a consequence to misinterpretations during the operation. The temperature control far away from the magnets is performed by Ni-NiCr thermocouples. The dependence of the measurement signal against a reference ice point ($T = 0°C$) is shown in Table 11.6.2. The temperature measurements within the magnetic field are carried out using Cu-CuNi (copper-constantan) thermocouples, which dependence on the temperature is also shown in Table 6.2.
Figure 11.6.1. Sheath options of thermocouples (NI, 2003)

Table 11.6.2. Electric voltage of the thermocouples Cu-CuNi and Ni-NiCr in millivolts as a function of the temperature in the range from 0°C to 400°C.

The temperature function is calculated from the electric voltage produced by the thermocouple with the following polynom:

\[ T \,[^\circ C] = A_0 + A_1.U[mV] + A_2.U^2[mV]. \]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Cu-CuNi</th>
<th>Ni-CrNi</th>
<th>Temperature</th>
<th>Cu-CuNi</th>
<th>Ni-CrNi</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>0.00</td>
<td>0.00</td>
<td>210°</td>
<td>9.74</td>
<td>8.54</td>
</tr>
<tr>
<td>10°</td>
<td>0.40</td>
<td>0.40</td>
<td>220°</td>
<td>10.29</td>
<td>8.94</td>
</tr>
<tr>
<td>20°</td>
<td>0.80</td>
<td>0.80</td>
<td>230°</td>
<td>10.85</td>
<td>9.34</td>
</tr>
<tr>
<td>30°</td>
<td>1.21</td>
<td>1.20</td>
<td>240°</td>
<td>11.41</td>
<td>9.75</td>
</tr>
<tr>
<td>40°</td>
<td>1.63</td>
<td>1.61</td>
<td>250°</td>
<td>11.98</td>
<td>10.16</td>
</tr>
<tr>
<td>50°</td>
<td>2.05</td>
<td>2.02</td>
<td>260°</td>
<td>12.55</td>
<td>10.57</td>
</tr>
<tr>
<td>60°</td>
<td>2.48</td>
<td>2.43</td>
<td>270°</td>
<td>13.13</td>
<td>10.98</td>
</tr>
<tr>
<td>70°</td>
<td>2.91</td>
<td>2.85</td>
<td>280°</td>
<td>13.71</td>
<td>11.39</td>
</tr>
<tr>
<td>80°</td>
<td>3.35</td>
<td>3.26</td>
<td>290°</td>
<td>14.30</td>
<td>11.80</td>
</tr>
<tr>
<td>90°</td>
<td>3.80</td>
<td>3.68</td>
<td>300°</td>
<td>14.90</td>
<td>12.21</td>
</tr>
<tr>
<td>100°</td>
<td>4.25</td>
<td>4.10</td>
<td>310°</td>
<td>15.50</td>
<td>12.63</td>
</tr>
<tr>
<td>110°</td>
<td>4.71</td>
<td>4.51</td>
<td>320°</td>
<td>16.10</td>
<td>13.04</td>
</tr>
<tr>
<td>120°</td>
<td>5.18</td>
<td>4.92</td>
<td>330°</td>
<td>16.70</td>
<td>13.46</td>
</tr>
<tr>
<td>130°</td>
<td>5.65</td>
<td>5.33</td>
<td>340°</td>
<td>17.31</td>
<td>13.88</td>
</tr>
<tr>
<td>140°</td>
<td>6.13</td>
<td>5.73</td>
<td>350°</td>
<td>17.92</td>
<td>14.29</td>
</tr>
<tr>
<td>150°</td>
<td>6.62</td>
<td>6.13</td>
<td>360°</td>
<td>18.53</td>
<td>14.71</td>
</tr>
<tr>
<td>160°</td>
<td>7.12</td>
<td>6.53</td>
<td>370°</td>
<td>19.14</td>
<td>15.13</td>
</tr>
<tr>
<td>170°</td>
<td>7.63</td>
<td>6.93</td>
<td>380°</td>
<td>19.76</td>
<td>15.55</td>
</tr>
<tr>
<td>180°</td>
<td>8.15</td>
<td>7.33</td>
<td>390°</td>
<td>20.38</td>
<td>15.98</td>
</tr>
<tr>
<td>190°</td>
<td>8.67</td>
<td>7.73</td>
<td>400°</td>
<td>21.00</td>
<td>16.40</td>
</tr>
<tr>
<td>200°</td>
<td>9.20</td>
<td>8.13</td>
<td>410°</td>
<td>21.62</td>
<td>16.82</td>
</tr>
</tbody>
</table>

Fit function polynom

<table>
<thead>
<tr>
<th>A0</th>
<th>A1</th>
<th>A2</th>
<th>Temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-CuNi</td>
<td>3.4834965</td>
<td>-0.21285</td>
<td>0°-410°C</td>
</tr>
<tr>
<td>Ni-CrNi</td>
<td>-0.4179542</td>
<td>-0.0201893</td>
<td>0°-380°C</td>
</tr>
</tbody>
</table>
In principle six (!) thermo-magnetic effects exist which can influence the temperature measurement. An overview and a detailed description of these effects is given in the article of [Kollie, et al., 1977] and [Eringen, 1980]. The effects can be categorised as:

a) transverse effects Righi-Leduc effect and Nernst-Ettingshausen effect;
b) longitudinal effects in a transverse field;
c) longitudinal effects in a longitudinal field.

Both, b) and c) cause changes in the thermal conductivity and the Seebeck coefficient of a material. Of these effects the Righi-Leduc and the two longitudinal effects of the Seebeck coefficient are besides the Nernst-Ettingshausen effect the most important in thermocouple thermometry in a magnetic field. In general appropriate design considerations and material choices have to be made before instrumenting a test section. Only the consideration of the afterwards named effects and order of magnitude estimations prevent long term and exhausting calibration measurements.

**The Nernst-Ettingshausen effect**

If a temperature gradient $\nabla T$ is perpendicular to a magnetic field $\mathbf{B}$ an electric field $\mathbf{E}$ will be produced perpendicular to both quantities related to Eq. (11.96). The magnitude of the electric field is determined by the Nernst-Ettingshausen coefficient $Q$, which is a material property like the thermal conductivity of a material.

$$\mathbf{E} = Q (\nabla T \times \mathbf{B})$$ (11.96)

The electromotive force $EMF$ produced given by the integral along the wire from zero to the length $l$:

$$EMF = \int_{0}^{l} Q (\nabla T \times \mathbf{B}) \, ds$$ (11.97)

The Nernst-Ettingshausen factor $Q$ for the four compounds appearing in the thermocouples Ni-NiCr and Cu-CuNi are shown in Table 11.6.3.

<table>
<thead>
<tr>
<th>Material</th>
<th>Q [10-11 V/(°C Gauss)]</th>
<th>$\mu_r$ magnetic permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (Cu)</td>
<td>0.27</td>
<td>1</td>
</tr>
<tr>
<td>Copper-nickel (CuNi)</td>
<td>0.71</td>
<td>1</td>
</tr>
<tr>
<td>Ni (alumel)</td>
<td>5.25</td>
<td>5</td>
</tr>
<tr>
<td>NiCr (chromel)</td>
<td>27.00</td>
<td>1</td>
</tr>
</tbody>
</table>

Let us consider a configuration in which a temperature gradient of $50^\circ$C per mm exists, the thermocouple has a diameter of 0.5 mm and the magnetic field strength is 2 Tesla ($2 \times 10^4$ Gauss). The thermocouple wires may have a length of 30 mm perpendicular to the temperature gradient and the magnetic field and they are insulated from each other by a magnesium oxide ceramic. A calculation which includes the heat conduction in the thermocouple yields the following astonishing result. The measurement error for a copper-constantan thermocouple for this set-up yields $1.015^\circ$Kelvin; for Ni-NiCr, however, on such a short length an error of $33.2^\circ$Kelvin is measured. Of course, the big assumed temperature gradient has been chosen to outline the measurement errors.
The Righi-Leduc effect

If a temperature gradient $\nabla T$ is oriented perpendicular to a magnetic field $\vec{B}$, a temperature gradient $\nabla T$ will develop transverse to $\nabla T$ and $\vec{B}$ according to Eq. (11.98).

$$\nabla T = S (\vec{B} \times \nabla T)$$  (11.98)

Herein, $S$ is the Righi-Leduc coefficient. However, Eq. (11.98) applies only if no heat flow occurs in direction of $\nabla T$, which is under adiabatic conditions. Similar to the Nernst-Ettingshausen effect a line integral for the temperature difference $\nabla T$ can be formulated, which reads to:

$$\Delta T = \oint_{\mathcal{C}} S (\vec{B} \times \nabla T) \, ds$$  (11.99)

The Righi-Leduc effect results finally in a indicated temperature in a magnetic field that is different from that indicated without a magnetic field. However, for a 1 m long Ni-NiCr wire in a magnesium oxide mantle exposed to a magnetic field of 2 Tesla and a transverse temperature gradient of 50°C/1 mm the error would be 45°C. The Righi-Leduc coefficient of nickel is $10^{-7}$/Gauss whereas the NiCr value was assumed to be infinitely small in the absence of data.

The Seebeck-effect

The Seebeck coefficient of metals is changed in the presence of magnetic fields. Such changes cause errors in the temperature measurement because the thermal electromotive force of a thermocouple $E_t$ is defined as line integral:

$$E_t = \int_{s_0}^{s_{lp}} [S_{ep} \nabla T] \, ds - \int_{s_0}^{s_{ln}} [S_{en} \nabla T] \, ds.$$  (11.100)

along the length of the positive branch ($l_p$) and the negative branch ($l_n$) of the thermocouple. The positive and negative Seebeck coefficients $S_{ep}$ and $S_{en}$ of non-ferromagnetic materials changes usually rather weak with the magnetic field [Kollie, et al., 1977]. For ferromagnetic materials the change is more expressed. The Seebeck coefficients for the two thermocouple pairs considered are shown in Table 11.6.4.

**Table 11.6.4. Seebeck coefficients $S_e$ from [Kollie, et al., 1977] and [Powell, et al., 1974]**

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_e [10^{-9} V/°C]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (Cu)</td>
<td>$\pm 1$</td>
</tr>
<tr>
<td>Copper-nickel (CuNi)</td>
<td>$3 \pm 1$</td>
</tr>
<tr>
<td>Ni (alumel)</td>
<td>$37 \pm 1$</td>
</tr>
<tr>
<td>NiCr (chromel)</td>
<td>$2 \pm 1$</td>
</tr>
</tbody>
</table>

Galvanomagnetic effects

Up to now only thermomagnetic effects are discussed. However, where magnetic fields appear also galvanomagnetic effects may appear due to the interaction of electric and magnetic fields and lead to a miscellaneous reading of a temperature signal. For example the Ettingshausen galvanomagnetic
effect, with the coefficient \( P_g \), produces a transverse temperature gradient in a transverse magnetic field \( \mathbf{B} \) and a current density \( j \) according to Eq. (11.101):

\[
\nabla T = P_g \left( \mathbf{j} \times \mathbf{B} \right)
\]

(11.101)

The coefficients \( P_g \) and the Nernst-Ettingshausen coefficient \( Q \) are related through the absolute temperature \( T \) and the thermal conductivity \( \lambda \) by Eq. (11.102):

\[
\lambda \ P_g = T \cdot Q
\]

(11.102)

11.6.2 Heat-emitting temperature-sensing surfaces (HETSS)

A technology to determine the heat flux transferred from a liquid metal flow through a thin walled structure is given by the heat emitting temperature sensing surface (HETSS) technique [Platnieks, et al., 1998] or [Patorski, et al., 2000].

The active element of the method is a simple surface that allows a well defined heat flux density to be generated in selected areas and the resulting temperature distribution to be recorded simultaneously. A HETSS represents the boundary between the solid and the liquid flow to be measured. Technically, the surface is an ensemble of electrically heated ohmic resistors whose electrical resistance and power dissipation can be measured with a definite spatial resolution. Measuring the potential difference \( \Delta \phi \) and the electric current \( I \) in each HETSS unit the dissipated power can be determined from the product \((\Delta \phi - I)\) of the two locations, while their ratio \((\Delta \phi/I)\) is the resistance between them, which depends on the temperature. The measured power release and the detected local resistance correspond in principle to the local heat transfer coefficient \( \alpha \), which is detected using this method. In order to measure this quantity several aspects have to be fulfilled. The surface resistor must be thin enough to ensure a large heat resistance in longitudinal direction and it must be backed by a thermal insulation in order to direct most of the heat through the liquid via the structural material.

The local heat transfer coefficient \( \alpha \) does not only depend on the local cooling capabilities of the flow but also strongly on the distribution of the heat flux density. Therefore, a sophisticated design of the foil shape is required in order to attain the heat flux distribution desired. Figure 11.6.2 illustrates the operation principle of a HETSS element.

Figure 11.6.2. (a) Technical sketch of a HETSS element used in the KILOPIE-MEGAPIE experiment. (b) Measurement principle of a HETSS element [Platnieks, et al., 2000].
The time dependent temperature $T(t)$ between two discrete points $m$ and $n$ of a segment of a HETSS element can be calculated:

$$T_{m,n}(t) = \frac{\phi_{m,n} - r_{m,n} \cdot \frac{T}{T_0}}{\alpha \cdot \frac{r_{m,n}}{T_0}} \cdot \frac{A_{m,n} \cdot k_m}{\lambda_s} \cdot \left( \frac{d_l + d_s}{\lambda_s} \right)$$

(11.103)

Herein, $\phi_{m,n}$ is the measured potential difference between the discrete points $m$ and $n$, $\phi_m$ the potential at $m$, $k_m$ the instrument resistance, $r_{m,n}$ the unheated HETSS unit resistance between the points $m$ and $n$, $T/T_0$ the ratio of the bulk temperature and the temperature of the unheated HETSS, $A_{m,n}$ the surface of the HETSS unit between the points $m$ and $n$, $d_j$ the thickness of the insulation and $\lambda_s$ its heat conductivity and finally $d_s$ is the thickness of the steel and its corresponding heat conductivity $\lambda_s$. The unheated HETSS unit resistance and the reference temperature are given by the following time integration:

$$r_{m,n} = \frac{1}{\tau} \int_{t=0}^{T} \left[ \left( \frac{\phi_m}{\phi_m(t)} \right)^2 \cdot \left( \frac{\phi_{m,n}}{\phi_{m,n}(t)} \right) \cdot \left( \frac{\phi_{m,n}(t)}{\phi_m(t)} \right) \cdot \left( \frac{\phi_{m,n}(t)}{\phi_{m,n}(t)} \right) \cdot \left( \frac{\phi_{m,n}(t)}{\phi_{m,n}(t)} \right) \right] d\tau$$

(11.104)

$$T_0 = \frac{1}{\tau} \int_{t=0}^{T} T(t) \ d\tau$$

Eqs. (11.103) and (11.104) reveal drastically the difficulties using the HETSS technology as a measurement tool. Besides the tremendous effort needed for the calibration of the device and the rather exact fabrication know-how the following uncertainties has to be quantified:

- accuracy of the measurement chain;
- detailed knowledge of the heat transport through the glue and the steel;
- heat losses through the environment and tangential to the foil (electric, convective and radiation losses);
- wetting behaviour of the liquid through the steel wall.

Despite these difficulties the HETSS technology represents a non-intrusive method to measure local temperatures and moreover allows simulating various heat loading scenarios of surfaces as they may appear in nuclear or chemical engineering applications, *c.f.* [Patorksí, *et al.*, 2001].

A challenge in context of the HETSS is the fabrication technology. In order to attain sufficiently high heat fluxes (up to 50 W/cm²) a thin nickel foil (around 50 µm thick) is glued to a 0.5 mm thick steel dish and is heated electrically by a DC current. The nickel heating foil can be specifically tailored, which allows to simulate different heat release scenarios. In order to get accurate results from the HETSS the element should employ adiabatic conditions to the ambient except for the test port. This can be achieved by a vacuum chamber or by an appropriate thermal insulation. The electric signals from the HETSS are obtained by pin contacts touching the nickel foil at discrete positions delivering a potential to the data acquisition. From these values the local heat flux can be calculated and the local temperature can be determined. Finally, the estimation of local convection heat transfer coefficient $\alpha$ is a result of ratio of the local heat flux to the difference of local surface temperature to the bulk temperature of the adjacent fluid. The spatial resolution perpendicular to the strips in the central part
of the foil is equal to the width of the strip. For a typical digital (16 bit, 1 digit = 40 \mu V) measurement equipment and appropriate integration time, the accuracy of the measurement in the middle can be predicted to approximately ±1% and at the periphery of the nickel foil to about ±10%.

11.7 Level meters

11.7.1 Direct contact sensors

The simplest system to detect a level in a container are simple electrode contact switch. Two states can be measured by using this system, namely if the contact height is arrived or not.

These kinds of systems are mostly simple self made constructions. The contact electrode technique takes advantage of the good electrical conductivity of the liquid metal. If an initially open electric circuit stressed by a voltage of 24 V is closed the moment where the liquid metal surface contacts the spike of the electrode the potential decreases. This can be captured by a reference circuit an gives the digital signal. In order to gather more information about the actual liquid level, it is necessary to install an array of these filling level meters or to traverse the level meter. A sketch of such a level meter and a photograph of a spark electrode are shown in Figure 11.7.1.

Figure 11.7.1. (a) Sketch of a spark electrode to detect a defined liquid metal level within a container and photograph of a level electrode used in the KALLA laboratory of FZK. (b) Swimmer arrangement to detect the level height using an electric potentiometer.

Other direct contact systems are swimmers, in which a lighter body is immersed in the container. Due to the high density of heavy liquid metals like, lead and its alloys, mercury, InGaSn and others different solutions are possible. The swimmer may be directly attached to a shaft connected with a resistive electronics or it may contain a magnet transmitting the level to a sensor outside. The output of such systems show a continuous signal which is proportional to the height of the liquid metal level within the container. A schematic drawing of a swimmer arrangement is shown in Figure 11.7.1(b). The advantage of the swimmer and the electrode systems is that they are cheap and reliable, because in such arrangements the detection system is decoupled from the high temperatures and the corrosive properties of the liquid.
Other direct level measurement methods are differential pressure gauges mounted to the container in such a way that one bore is connected to the bottom and the other branch is in the gas atmosphere above the liquid level. The liquid level corresponds to the measured pressure difference $\Delta p$ in the way:

$$\Delta p = \rho \cdot g \cdot \Delta h$$

(11.105)

where $\rho$ is the fluids density, $g$ the gravity constant and $\Delta h$ the liquid level height. This method is preferred especially for heavy liquid metals which have high density. A principal sketch is shown in Figure 11.7.2.

**Figure 11.7.2. Level measurement using differential pressure gauges**

![Diagram](image)

Another option to measure the liquid level in a container is offered by the bubbling technique, successfully performed in the CIRCE loop of ENEA. Here, bubbles of inert gas are injected via a Venturi tube into the liquid. While measuring the gas pressure in the bubble tube, the level can be recorded at the discrete position using only one sensor, which is not in direct contact with the liquid and thus temperature limitations for the use of such a kind do not exist. However, this type of level meter requires a calibration for the specific type of orifice at the outlet of the venture tube. Moreover, a simultaneously measuring thermocouple at the outlet of the tube is required accounting for the surface tension difference between the gas and the liquid at the different temperature levels. The technical realisation in a test–stand at the CRICE facility of ENEA is shown in Figure 11.3.1(c).

Other direct contact sensor types are ultra-sonic sensors connected to the volume of interest from underneath. For heavy liquid metals melting at temperatures above 120°C wave guides are necessary to decouple the ultra-sonic sensor from the hot medium. Generally, for this purpose two types of level and distance instrument are used in process industries: continuous and binary instruments. Both can be realised with ultrasound reflection techniques applying Eq. (11.106)

$$c = \lambda \cdot f = \frac{\Delta x}{\Delta t}$$

(11.106)

where $c$ is the sound speed, $\lambda$ the wave length, $f$ the frequency, $\Delta x$ the path length and $\Delta t$ the transit time. The time of flight (TOF) $\Delta t$ of a pulse sent by the device and reflected from the surface (or object) is measured and $c$ is known. Often the propagation of ultrasonic waves in air or inert gas is used. Then compensations for temperature and speed of sound changes due to vapours are needed. In dependence on the ultrasonic frequency (most devices work with ultrasonic frequencies from around ten to a few hundred kilohertz) a measurement range from millimetres to a few metres can be realised. Distance sensors operating in gas and using broadband ultrasonic transducers achieve a high local resolution in the direction of sound propagation. Accurate measurements down to a resolution of 0.25% can be expected. In latest developments of distance sensors with extremely high resolution, techniques of scanning acoustic microscopy are exploited [Kim, et al., 1999].
In many conventional ultrasonic distance sensors simple comparator circuits are used to detect the arrival of the reflected signal in a specific time window. Such distance sensors are employed in the automation of industrial processes, for example the positioning of work pieces, as well as in the chemical industry. Level measurement becomes difficult when more than one object creates echoes or the surface is rapidly changing its level, e.g. in case of a draining. For this reason intelligent ultrasonic sensors have been developed in the past, which have the capability to evaluate partial echoes in complex echo profiles. In [Eccardt, et al., 1995] a concept of signal processing for an intelligent distance sensor and its realisation is described. The main point is to separate real target echoes from misleading echoes by evaluating a set of suitable rules. Fuzzy logic techniques are used. The results are very important for level measurements. The spectrum of ultrasonic distance or level sensors reaches from relatively simple configurations to intelligent sensor systems. Endress & Hauser (Switzerland) has with the Prosonic system a large variety of continuous liquid/solid level instruments and limit switches on the market. Milltronics (Canada) offers a wide spectrum of level instruments; Honeywell (USA) offers distance and proximity sensors, which can be used for most level and presence detection applications. Many other producers are also on the market. Continuous ultrasonic level instruments compete with hydrostatic, radar and float technologies. About 20% of the level instruments are based on ultrasound. It is expected that the market share of ultrasonic instruments will increase since ultrasound is non-intrusive and the technology is well accepted. However, in the future radar techniques will gain more importance for the reasons of higher accuracy and dropping costs [Hauptmann, et al., 2002].

In the context of liquid metal application for the level detection the ultrasound technique was put in the direct contact sensor class, since especially in heavy liquid metal systems often a very clean atmosphere is used. In order to achieve this often the loop systems are filled against vacuum. In a vacuum, however, no acoustic signal can be transmitted and thus here a direct coupling to the medium via a waveguide is required [Zhmylew, et al., 2003].

11.7.2 Non-intrusive level sensors

Non-intrusive methods for the level detection in a container can be principally based on optic, acoustic, electromagnetic or nuclear methods. Since nuclear methods in terms of X-ray, γ-ray or neutron tomography are extremely expensive due to the high attenuation especially of heavy liquid metals, they are mostly not used to acquire the level height within a container. But, in principle this technique can also be applied for level measurement. The relations to detect the surface height are in principle given for these techniques in Section 11.5.2 for void measurement systems. In this context we concentrate ourselves on measurement principles based electromagnetic waves and radar waves. The optic sensors to detect surface waves are presented in the context of surface shape detection in the following chapter.

11.7.2.1 Electromagnetic level sensors

One of the simplest electromagnetic level sensing tools is based on the electromagnetic induction. Assume two plane parallel arranged coils, in which one is AC powered by a constant sinusoidal potential supply, the adjacent coil passive coil detects the sinusoidal excitation with a certain amplitude, depending on the distance between active and passive coil. The detection amplitude rapidly decreases if a well electrically conducting fluid rises in the container. Amplitude decrease is directly proportional to the height of the liquid level in the vessel. Such a system is schematically depicted in Figure 11.7.3, in which in an open tube two coils are inserted. For the level detection purpose mostly the support tube configuration is used, but, the support tube can also be placed directly in the neighbourhood of the
container. Then, however, the sensitivity of the device has to be calibrated new and is of course less than in the support tube configuration. Typically excitation frequencies of 45-400 Hz are used. In order to save money of a fast data acquisition system often the RMS value of the sensing coil is taken and subtracted from constant other potential in order to attain a level monitoring from 0% to 100%. Due to the decoupling of the sending and sensor device from the medium it can be used for arbitrary temperature ranges. In sodium such level meters worked up to 700°C, see [GEC Energy Systems, 1981]. Recently they have been set into operation in the THESYS loop of KALLA.

11.7.2.2 Radar distance measurement

The easiest way to measure the range of an object is to broadcast a short pulse of radio signal, and then time how long it takes for the reflection to return. The distance range $R$ is one-half the product of round trip time $\tau$ (because the signal has to travel to the target and then back to the receiver) and the speed of the signal. 

$$R = \frac{c_0 \cdot \tau}{2}$$

where $c$ is the speed of light in a vacuum. Since the speed of light is relevant the round trip times are very short. For this reason accurate distance measurement were difficult until the introduction of high performance electronics, with older systems being accurate to perhaps a few %. The receiver cannot detect the return while the signal is being sent out – there is no way to tell if the signal it hears is the original or the return. This means that a radar has a distinct minimum range, which is the length of the pulse divided by the speed of light, divided by two. In order to detect closer targets you have to use a shorter pulse length.

A similar effect imposes a specific maximum range as well. If the return from the target comes in when the next pulse is being sent out, once again the receiver cannot tell the difference. In order to maximise range, one wants to use longer times between pulses, the inter-pulse time. These two effects tend to be at odds with each other, and it is not easy to combine both good short range and good long range in a single radar. This is because the short pulses needed for a good minimum range broadcast have less total energy, making the returns much smaller and the target harder to detect. One could offset this by using more pulses, but this would shorten the maximum range again. So each radar uses a particular type of signal. Long range radars tend to use long pulses with long delays between them,
and short range radars use smaller pulses with less time between them. This pattern of pulses and pauses is known as the pulse repetition frequency (PRF), and is one of the main ways to characterise a radar. As electronics have improved many radar systems now can change their PRF.

Another form of distance measuring radar is based on frequency modulation. A frequency comparison between two signals is considerably more accurate, even with older electronics, than timing the signal. By changing the frequency of the returned signal and comparing that with the original, the difference can be easily measured. In these systems a “carrier” radar signal is frequency modulated in a predictable way, typically varying up and down with a sine wave or saw-tooth pattern at audio frequencies. The signal is then sent out from one antenna and received on another, and the signal can be continuously compared. Since the signal frequency is changing, by the time the signal returns to the aircraft the broadcast has shifted to some other frequency. The amount of that shift is greater over longer times, so greater frequency differences mean a longer distance, the exact amount being the “ramp speed” selected by the electronics. The amount of shift is therefore directly related to the distance travelled, and can be displayed on an instrument. This signal processing is similar to that used in speed detecting Doppler radar.

Usually radar systems to detect levels are made for the petrochemical industry, where large containers appear. In liquid metal systems with small dimensions the frequencies or the pulse repetition frequencies required to detect level distances in the range of millimetres are in the range of 15-300 GHz. Nevertheless using the frequency modulation technique a first test with a cheap sensor showed reasonable results with an accuracy of \( \pm 2 \) cm compared to a pressure gauge system.

11.8 Free surface measurements

In many nuclear applications heat fluxes appear causing temperatures beyond the sustainable limit of any structural material. A prominent example is the development of the free surface target for the planned international material irradiation facility IFMIF, where accelerated neutrons (\( >14 \) MeV) are shot directly on a lithium target, see e.g. [Ida, et al., 2002], [Jameson, et al., 2004] or [Ida, et al., 2005]. Another example also using a free lithium target is the SUPER FRS target planned to set into operation at GSI [Geissel, et al., 2003]. There, a pulsed uranium ion beam is accelerated and fragmented in a gravity driven vertical lithium jet. Regarding the nuclear heavy liquid metal application for waste transmutation the MYRRHA target is one of the examples of a free surface lead-bismuth cooled target, see e.g. [Abderrahim, et al., 2001].

Except for the nuclear application especially the metal casting companies face the problems of the instabilities occurring during the manufacturing process. As an example during the steel and alumina casting wavy surfaces can establish while the liquid metal flows in direction of the gravity field. If the wavy surface solidifies in an undesired manner the subsequent manufacturing process is significantly disturbed.

Therefore, techniques are required which allow to monitor and to control free surface flows. As liquid metals are opaque, corrosive and operate in most cases at relatively large temperatures, the discussion in this chapter concentrates mainly on non-intrusive optic or acoustic measurement devices.

11.8.1 Optic methods

One of the problems of liquid metals is that their optical reflection coefficient is close to one, which means that they are totally reflecting. This causes in most cases difficulties in using highly sensitive optical distance measurement methods. Commercially available photo-multipliers, in particular, are
too sensitive for a totally reflecting material. But, some of the liquid metals show wave length regimes, in which the reflectivity is significantly reduced. For example, liquid lead has a reflectivity of 0.94 at a wave length of $\lambda = 900$ nm. At $\lambda = 584$ nm corresponding to yellow light the reflectivity is decreased to 0.62, but it increases to 0.92 at $\lambda = 500$ nm again [Blaszkett, 1990]. Making use of this behaviour, e.g. by means of using a yellow filter triangulation methods, can be used. Consequently, before any optic method is used a detailed literature study or pre-experiments should be performed in order to take advantage of the individual properties of the metal used in the experiment.

The basic principle of active non-contact range-finding devices is to project a signal (radio, ultrasonic or optical) onto an object and to process the reflected or scattered signal to determine the distance. If a high resolution rangefinder is needed, an optical source must be chosen because radio and ultrasonic waves cannot be focused adequately. In addition to absolute distance measurement, laser range finding devices are traditionally used for 3-D vision, dimensional control, positioning or level control. Optical distance measurement methods can technically be put into three categories: interferometry, time-of-flight and triangulation methods. Considerable progress has been achieved during recent years by understanding the basic physical and information theoretical principles of range sensing. It appears advances in the design of lasers, integrated optics devices, emitter and receiver electronics will lead to further interesting developments. In this context, some laser range-finding techniques for industrial applications are briefly presented: triangulation, pulsed time-of-flight (TOF), phase-shift measurement and frequency-modulated continuous wave (FMCW) modulation. All these approaches are still further developed because the choice of the technique to be used depends mainly on the required application. Moreover, each of them presents limitations, which are discussed here.

Many applications do not allow contact or alterations to an object or surroundings to suit the measurement system, e.g. by changing the reflectivity of the surface with paint. These non-contact measurement techniques have found widespread use in heritage, environment modelling, virtual reality, robotics and many industrial fields. The true problem of these methods remains the fast and precise acquisition of the depth map with a large volume and in a natural environment. The most critical parameters of such systems are the depth measuring range $z$ and the depth resolutions $\delta z$. Figure 11.8.1 illustrates the measuring and resolution ranges that are covered by the existing industrial measuring systems. The highest absolute resolutions are achieved by interferometry, which reaches accuracies of $\lambda/100$ and can measure ranges up to 10 m using multi-wavelength techniques. Active triangulation can be used with high resolution from the millimetre range up to several meters. Here the accuracy depends mainly on depth of field and can be as high as 10 $\mu$m for small depths.

**Figure 11.8.1. Relative resolution of methods for optical shape and distance measurements from [Simoni, et al., 2002]**

![Figure 11.8.1. Relative resolution of methods for optical shape and distance measurements from [Simoni, et al., 2002]](image-url)
Finally, time-of-flight techniques allow measurement of depths in the range from tens of mm up to tens of km [Simoni, et al., 2002]. Here the depth estimation is an extreme challenge for time measurement and accuracy, being mainly dependent from mechanical and electronic drifts and independent from distance, is of the order of some mm.

The surface shape of liquid metal films can be imaged and digitised using the following basic components: a light source to define a specific pixel(s), such as an encoding-decoding process (e.g. triangulation, fringe and pattern projections and time of flight), a sensing device composed of a collecting lens and a photo detector that converts light energy to electrical signal, an analogue-to-digital converter, and finally a computer to process, display, and store the raw data [Rioux, et al., 1989].

The following reviews the basic concepts behind optical triangulation for three-dimensional digitising applications. It emphasises the critical elements of optimal design and the limitations related to the use of coherent light. It is shown, for example, that speckle noise is a fundamental limit for the position sensing of laser spot centroid. This has an impact on the choice of the position sensor geometry.

Of crucial importance is the choice of the light source. Conventional light sources can and are used for optical triangulation, but laser sources have unique advantages for 3-D surface imaging. One of these is brightness, which cannot be obtained by an incoherent emitter. Another is the spatial coherence that enables the laser beam to “stay in focus” when projected on the scene. Nevertheless, this property is limited by the law of diffraction, which is written here as the propagation (along the $z$ axis) of Gaussian laser beams:

$$\omega(z) = \omega_0 \left[ 1 + \left( \frac{\lambda \cdot z}{\pi \omega_0^2} \right)^2 \right]^{1/2}$$  \hspace{1cm} (11.108)

and, defining depth of field $D_f$ using the Rayleigh criterion gives:

$$D_f = 2 \cdot \pi \cdot \omega_0^2 / \lambda$$  \hspace{1cm} (11.109)

which shows that the depth of field $D_f$ is larger when the laser wavelength $\lambda$ is small (toward the blue) and/or when the laser beam spot size $\omega_0$ is large. A detailed analysis is given in [Rioux, et al., 1987].

11.8.1.1 Optical triangulation

On scattering, the spatial coherence of the laser light is lost, which means that the depth of field used at the projection can be useful only if the lens aperture is closed down at the collection. Otherwise the focused laser spot is imaged as a blurred disk of light on the photo-detector. A solution to this problem is to modify the conventional imaging geometry to conform to the Scheimpflug condition.

Essentially this geometry enables the photo detector surface to “stay in focus” with the projected laser light. Its construction is very simple when the focal planes of the lens are used. A typical triangulation measuring geometry is shown in Figure 11.8.2. A finely collimated laser source is used to probe the scene or object of interest. The probe works in continuous wave (CW) mode. A portion of the back-reflected light is focused onto a linear position sensitive device, PSD, placed at a fixed distance $d$ from the laser module. Indeed, it is known that a point on the projection axis located at $f$ (point $A$) will be imaged at infinity. Consequently the inclination angle of the photo-detector is defined
by drawing a line between that point and the principal point of the collecting lens (line 1). Similarly, on the other side of the lens, one knows that a point at infinity will be imaged at a distance \( f \) from the lens. The inclination and position of the photo detector are then obtained by constructing a line (line 2) parallel to line 1 passing through the point \( B \).

The position of the laser spot on the PSD is related to the distance of the object by the relation:

\[
\frac{d \cdot f_0}{p + f_0 \tan \gamma}
\]

where \( d \) is the distance between the collecting optics and the laser, \( f_0 \) is the focal length of the collecting optics, \( p \) is the spot position on the sensor, and \( \gamma \) is the deflection angle of the laser beam.

The accuracy in the distance measurement depends on depth and on the ability to define the spot position on the PSD. A simultaneous collection of chromatic information is also possible by using an RGB laser and splitting the back-reflected light into its colour components by means of a diffracting element, see e.g. [Baribeau, et al., 1992] A complete three-dimensional data set is obtained by scanning the laser beam in a raster mode over the object or scene of interest.

Sampling the shape along the \( x \) and the \( y \) axes is usually done in a straightforward manner [time or space interval, depending on the geometry of the photo detector(s)]. Sampling along the third dimension (\( z \) axis) often requires image pattern centroid location and interpolation. This is where coherence shows its limitation. Indeed, because of the coherent nature of the laser projection, the imaged laser spot on the photo detector(s) is corrupted with speckle noise. Here again, the geometry of the optical system and the wavelength of the light are the parameters.

Figure 11.8.2(b) shows how speckle noise adds to the uncertainty of an imaged laser spot. The origin of the modulation observed in the profile is related to the scattering of a pure wavelength when diffusion occurs at the surface of the object. Within the projected laser spot, each scatterer can be regarded as a coherent emitter, and because there are many of them within the area of illumination the resulting image is the coherent sum of spatially incoherent sources. The result is a random modulation multiplying the expected smooth light profile. [Baribeau & Rioux, 1991] formulated the relationship between the geometrical parameters as:

\[
\sigma^2 = \frac{\lambda^2 f_0^2}{2\pi (\phi \cos \beta)^2}
\]
where \( \sigma^2 \) is the position variance, \( \lambda \) the wavelength of the laser light, \( f_0 \) is the lens-CCD distance on the optical axis, \( \phi \) is the aperture of the collecting lens, and \( \beta \) is the Scheimpflug angle. When typical values are given for each parameter, the centroid uncertainty is found to be of the order of a few micrometers, and more interesting, the physical dimensions of the photo-sensor elements have no effect on that limit. Consequently, the larger the photo-sensors, the better are the performances of the 3-D digitiser in terms of sensitivity, speed, and depth of view. In practice, using wider photo-sensor elements means that the interpolation is done over a wider dynamic range. As an example, if the speckle noise limits is at 2 mm and the photo-sensor width is at 16 mm, one requires only 5 bits of numerical interpolation. On the other hand, if the photo-sensor width is 50 mm, 7 bits of interpolation are required. Notice that at least 2 bits are added to the ratio to reduce quantisation (or numerical) noise to a negligible level.

Some concluding remarks

Digitising shapes requires careful design consideration. For all active approaches including optical triangulation, the most critical element in order to achieve high-resolution imaging is the projection system, not the collecting system. In fact, in some cases it is found that optimum performances are obtained where the photo-sensor elements are of larger sizes. This is quite the opposite the case if only two dimensions are of interest, there only the use of a small sensor ensures a high location sensitivity.

11.8.1.2 Time-of-flight distance measurement

11.8.1.2.1 Pulsed TOF method

The laser pulse time-of-flight (TOF) distance measuring technique was originally used in military and surveying applications. It refers to the time it takes for a pulse of energy to travel from its transmitter to an observed object and then back to the receiver \((t_d)\). If light is used as energy source, the relevant parameter involved in range counting is the speed of light (~roughly \( c = 30 \text{ cm/ns} \)). A TOF system measures the round trip time between a light pulse emission and the return of the pulse echo resulting from its reflectance off an object. Using elementary physics, distance is determined by multiplying the velocity of light by the time light takes to travel the distance. In this case, the measured time is representative of travelling twice the distance and must, therefore, be reduced by half to give the actual range to the target. To obtain 1 mm accuracy, the accuracy of the time interval measurement should be 6.7 picoseconds.

Since a single pulse is adequate for the unequivocal determination of distance with centimetre precision and accuracy depends only weakly on distance, this method is particularly appropriate, for example, in applications involving distances longer than 1 m, applications where reflectors are not used and fast measurement applications such as scanning. In addition, averaging enables millimetre or even sub-millimetre precision to be achieved. The advantage of the TOF system arises from the direct nature of its sensing as both the transmitted and returned signals follow essentially the same direct path to an object and back to the receiver. To achieve these goals, the basic building blocks of a TOF range finder have to be realised in the form of high-performance integrated circuits. [Bosch & Lescure, 1995] provide an excellent review of absolute distance measurement in one of the SPIE Milestone volumes.

Principle set-up

A pulsed TOF distance measuring device consists of a laser transmitter emitting pulses with a duration of 5 to 50 ns, a receiver channel including a \( p-i-n \) or an avalanche photodiode, amplifiers, an automatic gain control (AGC) and timing discriminators. The emitted light pulse (start pulse) triggers
the time interval measurement unit, and the reflected light pulse (stop pulse) stops it. The distance to
the target is proportional to the time interval. A block diagram of a laser range finder is shown in
Figure 11.8.3(a).

![Figure 11.8.3. (a) Block diagram of a TOF laser range finder operating in the pulsed mode. (b) Timing jitter and walk.](image)

The selection of laser type depends on the intended measurement range and the required speed.
For laboratory purposes with small distance fast repetition frequencies are required. This restricts the
choice of the laser to laser diodes, which are capable to be used at rates of tens of kilohertz, the DH
type even reaches the Megahertz level [Amann, et al., 2001].

Problems of pulsed TOF measurements: Time jitter and walk, non-linearity and drift

The main sources of inaccuracy in laser rangefinders are noise-generated timing jitter, walk,
non-linearity and drift. Typical noise sources include noise generated by the electronics, shot noise
caused by the background radiation induced current and shot noise created by the noise of the signal
current. Jitter in timing determines mainly the precision of the range measurement. The amount of
timing jitter is proportional to noise amplitude (root mean square ~rms) and inversely proportional to
the slope of the timing pulse at the moment of timing (du/dt). A single-shot resolution of 1 cm can
typically be achieved with a good signal (SNR = 100, signal to noise ratio) using the 100 MHz
bandwidth of the receiver channel. However, precision deteriorates as the distance increases and the
pulse amplitude decreases proportional to the square of the distance [Määttä, et al., 1993]. Pulse
amplitude and shape variations create timing error in the time-pickoff circuit and that error is called
walk error. Jitter and walk in leading edge timing are shown in Figure 11.8.3(b).

The time discriminator is a very important part of a precision time measurement system. The task
of the discriminator is to observe time information from the electric pulse of the detector preamplifier
and to produce a triggering signal at the right instant. The choice of time derivation method depends
on the desired time resolution, counting rate and required dynamic range of the pulse. Commonly used
principles in discriminator design include leading edge timing (constant amplitude), zero crossing
timing (derivation), first moment timing (integration), and constant fraction timing. Constant fraction
discrimination (CFD) compensates with idealised pulse shapes for walk caused by both amplitude and
rise time and is commonly used in the TOF measuring units of laser range finders. The principle behind the operation of CFD is the search for an instant in the pulse when its height bears a constant ratio to pulse amplitude. The occurrence of this point produces a triggering pulse. The constant fraction instant can be examined with a high gain differential emitter-coupled logic (ECL) comparator, which amplifies the difference of the attenuated and the delayed pulses [Maier & Sperr, 1970]. CFD compensates for walk caused by amplitude and rise time, but not for walk caused by non-linear shape variations. Zero crossing and first moment timing compensate for amplitude variations, while leading edge timing fails to compensate for any variation described.

The transmitter, gain-control and time-interval measurement units are also critical for the accuracy of the system. The transmitter should be able to produce a stable laser pulse shape. This may call for the temperature stabilisation of the diode. The dynamic phenomena of the laser diodes, relaxation oscillations, should also be considered when designing the pulsing scheme as they may easily lead to significant changes in laser pulse shape. Gain control is needed to adjust the dynamics of the timing pulse to that of the timing discriminator. The amount of control needed depends on the measurement range, construction of the optics and reflectivity variations of the object. An adjustable optical attenuator at the receiver optics can be used to realise gain control. The advantage of this method over electrical gain control is its delay stability over a wide control range. Recently, the dynamic range of electronic gain control methods has increased quite remarkably, [Ruotsalainen, et al., 1999]. The time interval between the start and stop pulses is measured with the time-to-digital converter (TDC), which is a fast, accurate and stable time-interval measuring device that uses, e.g., a digital counting technique together with an analogue or digital interpolation method [Räisänen, et al., 1998]. The single shot resolution of the TDC is typically better than the noise generated timing jitter.

The final precision of the distance measurement can be greatly improved by averaging, with the improvement being proportional to the square root of the number of results averaged. Thus, by averaging 100 successive measurements, the final resolution can be improved to the tenth of millimetre level, the corresponding measurement time being 1 ms with a pulsing rate of 100 kHz, for instance. If the statistical error is averaged to a negligible level, the accuracy of the system is defined by its systematic errors such as nonlinearity in the time interval measurement scale and drift.

11.8.1.2.2 TOF laser phase-shift distance measurement

In a phase-shift distance measurement device, the optical power is modulated with a constant frequency. The basic operating scheme of the device is shown in Figure 11.8.4. A sine wave of frequency $f_{\text{rf}}$ generated by the main oscillator modulates the dc-current of the laser diode. After reflection from the target, a photodiode collects a part of the laser beam. Measurement of the distance $D$ is deduced from the phase shift $\Delta \phi = 2\pi f_{\text{rf}} \Delta t$ between the photoelectric current and the modulated emitted signal:

$$D = \frac{1}{2} c \frac{\Delta \phi}{2\pi} f_{\text{rf}}$$

(11.112)

where $c$ is the speed of light in free space and $\Delta t$ the time of flight (TOF).

When $\Delta \phi = 2\pi$, the unambiguous distance measurement is limited to $\Lambda = c f_{\text{rf}}/2$. To ameliorate the accuracy of this set-up, the phase shift is not directly measured at the working high frequency but at an intermediate frequency $f_{\text{if}} = |f_{\text{rf}} - f_{\text{local}}|$ using a heterodyne technique that preserves the phase shift versus distance. The signals of the two mixers outputs are filtered by a passband circuit tuned on $f_{\text{if}}$ and with a $\Delta f_{\text{if}}$ bandwidth.
When the target area is as large as the area illuminated by the transmitter, the received signal power $P_R$ is given by the relationship:

$$P_R = T_T \cdot T_R \cdot \frac{\rho_L}{\pi} \cdot P_0 \cdot \cos \theta \frac{A_R}{D^2}$$  \hspace{1cm} (11.113)

where $P_0$ is power output of the laser diode, $T_T$ the collection and transmission efficiency of transmitter, $T_R$ the transmission of the receiver optics, $\rho_L$ the Lambertian reflection coefficient of the fluid, $\theta$ the laser beam incident angle on the surface, $A_R$ the area of receiver lenses.

Only the Lambertian component is used for the calculation of the photoelectric signal; the specular component is ignored in Eq. (11.113). As a matter of fact, the term $\frac{\rho_L P_0}{\pi}$ is the power intensity (~ in watts per steradion) reflected perpendicular to the liquids surface. From this equation it becomes obvious that the method is not able to operate a high Lambertian reflection coefficients (>0.8). For the use in liquid metals specific adapted wave lengths of the laser and appropriate filter systems must be applied. Also for these methods a careful error analysis must be performed, which is in principle described below, for a more specified information on this technique the related literature cited gives sufficient information.

**Error analysis**

a) **High levels of the rf channel**

The power budget shows that the ratio $P_R/P_0$ may vary with a factor greater than 1000 if the distance $D$ varies for example from 1 to 10 m. Thus, when the photoelectric signal amplitude varies with a factor 1000, the phase-shift error $\delta \varphi$ introduced by this variation must be less than 0.1° for an error distance measurement $\delta D$ of 2.5 mm. But, with large amplitude of the useful signal, distortion and clipping introduce phase-shift errors. To avoid this error, the first solution is the defocusing of the photodiode, so that it receives less light when measured distances are small. A second solution is increasing the feedback of the mixer to avoid distortion and clipping [Perchet, et al., 1997].

b) **Intermediate frequency shift**

With a low-power laser diode, a narrow bandwidth amplification improves the signal to noise ration (SNR). For a white noise at the input, the output of a pass band second-order filter presents a noise-equivalent bandwidth $B_n$ given by the relationship [Cherry &Hooper, 1968]:

---

Figure 11.8.4. Block diagram of a phase shift laser distance measurement using a heterodyne technique
Thus, the rms noise of the useful signal is proportional to the square root of the bandwidth $\Delta f_{IF}$. Because of symmetry, it can be supposed that the frequency drift $\delta f_{f_i}$ or $\delta f_{f_o}$ of one oscillator balances the drift of the other one. No error is present if the two intermediate frequency filters are identical on reference channel and signal channel. But if the value of the bandwidth is too narrow, we must take into account the device mismatch effects introduced in intermediate frequency tuned circuits by the frequency drifts of $f_{f_i}$ and $f_{f_o}$. For example, for Rauch filter structure, the quality factor $Q = f_d/\Delta f_{IF}$ and the tuned frequency $f_{IF}$ mismatches are imposed by the presence of capacitance mismatches.

However, to guarantee the resolution, the best method consists of keeping the value of the intermediate frequency constant by a phase-locked loop technique. In [Payne, et al., 1992] and [Goldmann, et al., 1997] 20, 100 m distance measurement to a retro-reflector is obtained (~i.e., with a good SNR) with errors of less than 50 $\mu$m (!). The stable $f_{d} = 1.5$ GHz modulating frequency is generated from the 15th harmonic of a 100 MHz output of a Rubidium atomic clock.

c) Influence of crosstalk

Electrical crosstalk between the transmitter and the receiver produces another important error. When the photoelectric signal and the modulation current of the laser diode have the same frequency $f_{rf}$, the synchronous leakage $v_{crosst}$, arising from the modulation current source, is superimposed on the working photoelectric signal $v_{ph}$. The two signals are added vectorially. The trans-impedance amplifier associated with the photodiode must be shielded to exclude undesired external signals. However, because the influence of the crosstalk cannot be totally removed with shielding techniques, different methods have been proposed. To remove the effects of this field leakage, the gain switch of a laser diode is used as a light comb generator, and an avalanche photodiode (APD) selects the second harmonic of the photoelectric signal [Seta & Ohishi, 1987]. Another method, based on the use of a Pockels cell, has been proposed to obtain a measured signal at a frequency that is a multiple of the modulation frequency, although its implementation is still rather in its infancies [Lescure, et al., 1991].

The crosstalk errors at the modulation frequency $f_{rf}$ determine the minimum signal-to-induction ratio necessary to obtain a given accuracy. For example, to limit the maximum error phase shift $\delta\phi$ to 0.1°, the amplitude ratio of the photoelectric signal on the leakage signal must be 600 (~55 dB). Because the induced signal is “masked” by the electrical noise, the SNR must be higher than 55 dB. This condition is difficult to satisfy when the frequency modulation $f_{rf}$ of a low-power laser diode is higher than 10 MHz. The maximum distance measurement error $\delta D_{max}$ is independent from the modulation frequency and increases with the square of the distance, c.f. Eq. (11.113). Because the photoelectric current and crosstalk are added vectorially, a periodic error is obtained versus distance $D$. In this way, this error can be compensated. This method was proposed initially by [Müller, et al., 1997].

To determine a rough estimation of the crosstalk between the driver laser and the photodiode, a model of fictitious sources of perturbation at the input of the transimpedance amplifier has been proposed by [Bosch & Lescure, 1997]. The coupling is represented by the mutual capacitance and the mutual inductance. These models show the advantage of using an APD. Indeed, the gain of the primary photoelectric current occurs inside the semiconductor crystal itself, and it can be assumed that the crosstalk becomes superimposed on the output signal only when the signal has been amplified. But, as APD areas are small, this gives a small field of view of the receiver. For 3-D vision, if only the laser beam is deflected by micromirrors, a large field of view of the receiver is necessary, when no scanning mirrors are used in the receiver channel. A large p-i-n photodiode surface gives such a field
of view. So, the large photodiode capacitance increases the time constant at the input of signal channel, that reduces the bandwidth and/or the phase margin of the transimpedance amplifier. One solution is to compensate the photodiode capacitance by a tuned circuit. This technique is possible because the phase-shift distance device is working at one frequency $f_d$ only.

**Some final remarks**

Distance measurement by the phase-shift technique is a good method to obtain a resolution of some tens of millimetres with non-co-operative targets. For co-operative targets, i.e. sharp liquid waves, the resolution can be better than 50 μm, with high-frequency modulation. Because the photoelectric current is a sine wave, a photodiode with a large area can be used to achieve a wide angle of the field of view. In this way, it is possible to scan the laser beam by micro-mirrors, enabling compactness and low cost. Nevertheless, this method requires a large angle of view to the liquid metal surface, which is not given in some applications. Moreover, a careful look has to be taken the fluid used in the individual experiment and the corresponding wave length of the laser.

### 11.8.1.2.3 TOF optical radar

Optical distance measurement with the optical radar technique, often called FMCW technique, has been used in various applications such as non-contact surface profiling, fibre optic sensing, reflectometry, positioning and tomography. The interest in the FMCW technique is due to the large dynamic range and the high resolution, particularly at short range sensing. Because of the recent progress in the area of laser diode technology, high performance FMCW ranging systems can currently be realised with electronically tuneable laser diodes. A comprehensive description of this technique may be taken from the articles of [Beheim & Fritsch, 1983], [Strzelecki, et al., 1988], [Slotwinski, et al., 1989], [Burrows & Liou, 1990] and [Diekmann, 1994]. Below the operation principle of the FMCW technique is described and the system performance achievable with laser diodes at the current state is discussed.

The principal setup of an optical FMCW radar system is illustrated in Figure 11.8.5(a). The optical power from a frequency modulated laser diode, the instantaneous frequency of which is periodically shifted by $\Delta f$, is used as probing signal as shown in Figure 11.8.5(b).

The periodic and linear frequency chirp may practically be performed by applying a saw-tooth bias current to the modulator section of the wavelength-tuneable laser diode. The laser output passes an optical isolator to avoid deteriorations of the laser frequency by reflections and is then sent simultaneously to the object and the reference mirror, and the reflected signals are then superimposed in a square law detector diode. Owing to the detection process that is proportional to power, i.e. the amplitude squared, both signals are mixed in the detector and the main ac component of the electrical output is at the frequency difference $f_d$ of the two optical signals. The detector output is fed into an amplifier-limiter so that unintentional amplitude modulation is suppressed. Finally, the intermediate frequency $f_d$ of the reflected signals is measured with a frequency counter. Due to the square law mixing process the amplitude of the detector output at $f_d$ is proportional to the amplitudes (not the powers) of the object signal and the reference, respectively. Accordingly, the dynamic range of the FMCW technique is twice as large as that of the pulse radar technique, where the electrical signal is proportional to the object signal power.

The distance difference between object and reference mirror $R$, which is the relevant quantity to be determined, is proportional to $f_d$ as indicated in Figure 11.8.5(b). Since the round-trip delay time $t$ of the object signal is given as:
\[
\tau = \frac{2R}{c}
\]

where \(c\) is the light velocity, the intermediate frequency amounts to:

\[
f_{ig} = \Delta f \cdot \tau / t_m = 2 \cdot \Delta f \cdot R / c \tau m
\]

where \(t_m\) denotes the ramp period, which is typically of the order 0.1 to 1 ms. Accordingly, the distance sensing is done by an electric frequency measurement (usually in the kilohertz regime), while in the case of the more popular pulse radar, the delay time is measured directly. As the ramp period can be chosen arbitrarily, the FMCW radar can determine \(t\) values in the picosecond range, according to millimetre distances \(R\), by simply performing a frequency measurement in the kilohertz regime. Consequently, no high-speed electronic is required to determine delay times even in the subpicosecond range.

**Figure 11.8.5.** (a) Schematic set-up of an optical radar using a tuneable laser diode as light source. Instantaneous optical frequencies versus time of the object and reference mirror optical signals. (b) In case of a linear optical frequency ramp, the intermediate frequency \(f_{ig}\) is constant between \(t_1\) and \(t_2\). (c) In case of a non-linear optical frequency ramp, a chirping intermediate frequency occurs.

**Limitations**

Unfortunately, the frequency modulation response of a laser diode is, in general, non-uniform against the modulation frequency, so that a linear optical frequency sweep cannot be realised by a linear modulation of the control current. In addition, the frequency versus control current characteristic is also in general non-linear. As a consequence, deviations from the linear ramp as shown in Figure 11.8.5(c) usually occur that, in turn, lead to a variation of the intermediate frequency \(f_{ig}\). While the total phase difference \(\phi\) as indicated by the shaded areas in Figures 11.8.5(b) and 11.8.5(c) is still proportional to \(\tau\) and the distance \(R\) as long as \(t < t_m\), the variation of \(f_{ig}\) during each ramp increases the total intermediate frequency bandwidth and, consequently, the noise level that finally limits the accuracy. A usual technique to eliminate the effect of the nonlinear frequency ramp is to use simultaneously a reference Line, so that the ratio of distance \(R\) and the length of the reference line is independent of the linearity of the frequency ramp. Various schemes have been presented to linearise the optical frequency sweep of the laser diodes, which commonly utilise a reference delay line to determine the variations of the intermediate frequency \(f_{ig}\).
The maximal measurable distance of an optical radar system based on laser diodes is limited by the coherence length of the laser diode. The finite value of the latter, which typically is of the order of several tens of meters is a consequence of the laser diode phase noise that also determines the spectral line width. Correspondingly, laser diodes with narrow line-widths within the frequency sweep range are best suited for the measurement of longer distances.

Experimentally, high resolution in the submicrometre regime has been demonstrated with diode laser FMCW ranging systems [Burrows & Liou, 1990]. Using widely continuously tuneable laser diodes with $\Delta f$ of 500 GHz, a spectral line width of 25 MHz, and a repetition period $t_m$ of 10 ms, the one-shot relative accuracies for distances of 1 m and 1 cm down to millimetres, respectively, amount to $4.3 \times 10^{-5}$ and $2.7 \times 10^{-4}$ [Diekmann & Amann, 1995]. These results clearly prove the high performance of this technique for the accurate and fast measurement of short distances and, considering the large modulation bandwidth of laser diodes, make this technique also well suited for 3-D viewing systems.

### 11.8.1.3 Projection techniques

The demands of the automobile industry to manufacture precise mostly reflecting surfaces in order to allow for a fully automatic production process controlled by manipulators led in the past decade to the development of rapid 3-D surface detection techniques. Most of these techniques are based on projection of the object on an observing CCD camera. An overview and the related literature on new developments in fast 3-D surface quality control can be found in the article by [Leopold, et al., 2003]. In general several reflection techniques can be used such as structured lighting reflection, coded lighting or colour lighting. Most of the can only be used to objects at rest. Flowing heavy liquid metals, however, reveal a spectrum of motion on different time scales, which requires a fast acquisition technique. Thus the information to describe the surface is not only a function of the geometry but also of the time.

Due to this fact mostly fringe projection systems are used for acquiring rapidly three-dimensional surface information. These systems are robust against surface texture and reliable. Using fringe projection even objects with large surface gradients and large extensions in the direction of recording can be captured. The fringe projection also allows to measure shapes or films without any gradients, which is impossible using the stereo-matching [Böhm, 2001].

The fringe projection is based on the light sheet technique as principally shown in Figure 11.8.6. A single line is projected on the on the liquid metal film (the object) and observed under another angle by a camera. The deformation of the line yields parallax and thus the three-dimensional form along the line. In order to acquire a surface many lines are projected in a dense distance from each other onto the object. In order to obtain a definite information all fringes are not projected simultaneously onto the surface. They are rather projected in a defined time series onto the surface as a binary pattern. Most of the systems used in the manufacturing industry use for the encoding the Gray sequence, in which for $n$ lines only $ldn$ patterns are projected on the liquid surface. This Gray code sequence solves very roughly the correspondence between the projector co-ordinates and the camera co-ordinate on the pixel level. In order to attain a sub-pixel accuracy another pattern sequence must be projected on the surface. Most efficiently operates the phase shifting technique, which is described below and schematically depicted in Figure 11.8.7, but two general disadvantages of the phase shifting technique should be mentioned in this context.

The phase shift method assumes a sinusoidal representation of the fringe pattern on the sensor (which is the camera), which is not given in a frame based projection system. This yields to measurement errors. The sinusoidal form of the fringe pattern must first be generated. This can be
achieved by a defined defocusing of the projection unit. This has the disadvantage that the defocusing only leads in a certain distance of the object to the projector to the desired result. If the distance of the object surface varies strong in camera direction, then the fringe pattern will be depicted only in a few areas of the object sinusoidal in many others however not. A second option to generate a sinusoidal pattern of frame projectors offers the use of an optic low-pass filter in front of the projector. But this is only possible in direction of the fringes so that a cross-projection is not longer feasible.

A second disadvantage of the phase shift technique is the analysis of the correspondence of one camera pixel to the projected fringe line. Using the phase shift technique an odd or even but in any case a natural pixel co-ordinate of the camera is correlated with a sub-pixel co-ordinate of the projector. If several cameras observe the same fringe sequence a direct pixel-to-pixel correspondence between the cameras can be established.

In order to avoid the disadvantages of the phase shift technique the line shift method was developed [Gühring, et al., 2000]. The line shift method is not based on the assumption of a sinusoidal depiction of the fringe pattern. Here, for each projected fringe line separately the centre in the picture is determined, see Figure 11.8.7. This allows correlating natural numbered projector co-ordinates with sub-pixel co-ordinates of the camera and thus enables a direct coupling of the frame measurements of several cameras, which observe the same fringe sequence. Due to this fact an increased redundancy is obtained and a higher accuracy is ensured. Another advantage of the line shift technique is a better compensation of eventual reflectivity changes at the liquid metal surface. Unfortunately, this new technology has currently low temporal resolution in the range of 10 Hz. But due the increasing computer technology and speed in the near future a more efficient system can be expected.

11.8.1.3.1 Fringe projection

In the fringe projection technique, a known optical fringe pattern is projected onto the surface of interest; the distribution of the fringe pattern on the surface is perturbed in accordance with the profile of the test surface, thereby enabling direct derivation of surface profiles. Phase shifting techniques [Quan, et al., 2001] are usually employed by projecting several fringe patterns with prescribed phase shift; however, these techniques are restricted to static objects. In many cases, 3-D surface profiling is required for vibrating objects or for objects with continually changing profile. With the availability of high-speed digital recording, it is possible to record projected fringe pattern with rates exceeding 10000 frames per second (fps). Recently several methods have been reported to retrieve the phase map from these images. [Huang, et al., 1999] developed a colour-encoded fringe projection technique to obtain the phase map by separating fringes with different colours followed by phase shifting. Previous
investigations by [Tay, et al., 2003] have shown that fast Fourier transform (FFT) with carrier fringe method is another effective approach. It requires fringes with high spatial frequency acting as a carrier. With proper filtering in frequency domain, the contour can also be evaluated. These two approaches are based on a similar concept in getting the phase map in spatial co-ordinates along the time axis. [Pawlowski, et al., 2002] developed a novel approach to retrieve point-by-point phase values using 1-D FFT along the time-axis. The spatial phase map at a certain instant can be obtained by combining the phase value of each point. Unlike Pawlowski’s method of 1-D FFT, the current simple but robust trend is to retrieve point-by-point phase values along the time-axis [Tay, et al., 2004]. This method utilises a liquid crystal display (LCD) fringe projector and a high-speed CCD camera with telecentric gauging lens. High quality linear fringe patterns are projected on a vibrating object and the fringe patterns are imaged consecutively by a high-speed CCD camera. Applying phase scanning method initially reported by [Li, et al., 2001] on these fringe patterns, the surface profile at any instant, as well as the amplitude and frequency of the vibration, can be reconstructed.

The shape measurement based on the use of long working distance microscope, the LCD fringe projection and the phase-shifting methods allows even to measure large height measurement ranges up to 500 mm [Quan, et al., 2001] with accuracies in the range of microns.

Operation principle

Figure 11.8.8(a) shows the schematic layout of the projection and imaging system. With normal viewing, the phase change due to height \( h \) is given by:

\[
\frac{h}{d} = \frac{S}{d} = \frac{\phi}{2 \cdot \pi \cdot f_0} = k \cdot \phi
\]

(11.117)
where $L$ is the distance between the LCD projector and the reference plane, $d$ is the distance between the projector and camera axis, $f_0$ is the spatial frequency of the projected fringes on the reference plane and $k$, which can be obtained by calibration, is an optical coefficient related to the configuration of the system. $\phi$ is the phase angle change which contains the surface height information.

Figure 11.8.8. (a) Schematic layout of the projection and imaging system in the fringe projection technique. (b) Top view of the camera system.

When a vertical sinusoidal fringe pattern is projected onto a moving three-dimensional surface, the distribution of the grating is perturbed by two factors, the motion or deformation of the surface and the initial profile of the test surface, when it is not deformed. The mathematical representation of the intensity distribution $I$ captured by a CCD camera is governed by Eq. (11.118).

$$I(x,y,t) = a(x,y,t) + b(x,y,t) \cdot \cos[2\pi f_0 x + \phi_0(x,y) + \phi(x,y,t)]$$

where $a(x,y,t)$ and $b(x,y,t)$ are the background and modulation factor, respectively, $\phi_0(x,y)$ is an initial phase which contains the shape information, and $\phi(x,y,t)$ is a time-dependent phase function related to the object vibration or deformation. $a(x,y,t)$ and $b(x,y,t)$, which are also functions of time, are both slowly varying functions. Hence, $a(x,y,t)$ and $b(x,y,t)$ can be regarded as constants in one period of intensity change. This assumption is of limiting nature with respect to the temporal resolution of fringe projection technique. Several images or frames are required, in which the surface shape is assumed to be constant. Assuming a frame rate of 250 frames per second as in the Tay, et al. experiment and at least eight frames, which are required to define the shape a temporal resolution of at maximum 30 Hz of the surface can be achieved.

If the amplitude of the surface motion is large enough, the variation of $\phi(x,y,t)$ will be larger than $2\pi$, which implies more than one period intensity change. In most cases, this assumption can be satisfied by proper selection of carrier fringe frequency, projection angle and imaging area. With this assumption, the detectable maximum and minimum values of intensity within one period of intensity change at a certain point $P(x_p, y_p)$ on the test surface can be written as:

$$I_{\text{max}}(x_p, y_p) = a(x_p, y_p) + b(x_p, y_p)$$
$$I_{\text{min}}(x_p, y_p) = a(x_p, y_p) - b(x_p, y_p)$$

(11.119)
Subsequently Eq. (11.118) is rewritten as:

\[ I(x_p, y_p, t) = \frac{1}{2} \left[ I_{\max}(x_p, y_p) + I_{\min}(x_p, y_p) \right] + \frac{1}{2} \left[ I_{\max}(x_p, y_p) - I_{\min}(x_p, y_p) \right] \cos \Phi_p(x_p, y_p, t) \]  

(11.120)

where:

\[ \Phi_p(x_p, y_p, t) = 2\pi \cdot f_0 x_p + \phi_0(x_p, y_p) + \phi(x_p, y_p, t) \]  

(11.121)

Hence the phase value can be expressed as:

\[ \Phi_p(x_p, y_p, t) = \arccos \left( \frac{2I(x_p, y_p, t) - I_{\max}(x_p, y_p) - I_{\min}(x_p, y_p)}{I_{\max}(x_p, y_p) - I_{\min}(x_p, y_p)} \right) \]  

(11.122)

As the first two terms in Eq. (11.121) are constants on the time-axis, the relative phase variation due to surface deformation at point \( P \) can be obtained as:

\[ \phi(x_p, y_p, \Delta t) = \Phi_p(x_p, y_p, t_2) - \Phi_p(x_p, y_p, t_1) \]  

(11.123)

At a certain time \( T \), the phase map representing the contour of the surface can be expressed as:

\[ \Phi(x, y, T) = 2\pi \cdot f_0 x + \phi_0(x, y) + \phi(x, y, T) \]  

(11.124)

where \( \phi(x, y, T) \) denotes the phase which is related to the surface deformation at instant \( T \). Both phases \( \phi(x_p, y_p, \Delta t) \) and \( \phi(x, y, T) \) are wrapped phase values, as \( \Phi_p(x_p, y_p, t) \) given by Eq. (11.122) is within 0 to \( \pi \). For unwrapping, the values of \( \phi \) at each point are converted from \([0, \pi]\) to \([0, 2\pi]\). The phase values after conversion are determined by two factors, namely direction of deformation and the slope of intensity \( \partial I/\partial t \) along the time-axis. Table 11.8.1 shows the details of the conversion. Unwrapping the phase values \( \phi(x_p, y_p, \Delta t) \) given by Eq. (11.124) along the time-axis is a 1-D problem; retrieving the continuous phase values from \( \phi(x, y, T) \) in Eq. (11.124) is a 2-D unwrapping problem, where numerous unwrapping algorithms are applicable, see e.g. [Ghiglia & Pritt, 1998].

### Table 11.8.1. Conversion of phase values from \([0, \pi]\) to \([0, 2\pi]\)

<table>
<thead>
<tr>
<th>Phase value in ([0, \pi])</th>
<th>Direction of deformation</th>
<th>Slope of intensity along time axis ( \partial I/\partial t )</th>
<th>Phase value in ([0, 2\pi]) after conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi )</td>
<td>Forward</td>
<td>( \geq 0 )</td>
<td>( 2\pi - \phi )</td>
</tr>
<tr>
<td></td>
<td>Backward</td>
<td>( &lt; 0 )</td>
<td>( \phi )</td>
</tr>
</tbody>
</table>

**Experimental resources**

For a free surface experiment a vertical sinusoidal fringe pattern is projected onto the fluid by a programmable LCD projector. The fringe patterns are captured at right angle to the surface at rest by a high speed CCD camera, e.g. KODAK Motion Corder Analyzer, SR-Ultra. Using a telecentric gauging lens ensures that the magnification of telecentric lens is independent of the working distance, in
contrast to conventional lenses. It remains constant regardless of the object distance from the camera. This reduces magnification error due to the deformation and greatly extends gauging depth of field. With this special lens, the positions of a moving object in the image plane remain the same, while only the fringe pattern is shifted periodically. The pitch of the fringe pattern and the angle of projection are selected according to the amplitude of surface deformation.

At the start-up the coefficient $k$ in equation must be determined in a calibration procedure. Therefore, the fluid surface is set to a known distance in the $z$-axis and the corresponding phase difference on the surface for different heights is determined by the conventional four-step phase shifting method.

In a next step the surface of interest can be investigated. Therefore, the minimum and maximum intensities occurring at each point must be determined. The extreme positions of surface deformation vibration are readily identified by the computer since the first derivative of intensity $\frac{\partial I}{\partial t}$ of most pixels in the image changes sign (either from positive to negative or vice versa). If this is performed the real test run can start.

For each pixel, several data points along the time axis are obtained. Figure 11.8.9(a) shows the grey value variation of a discrete point of a polished coin in the [Tay, et al., 2004] experiment, which was defined vibrated on a table. The extreme positions of the vibration are encircled in Figure 11.8.9(b). The corresponding wrapped phase values of this experiment are presented in graph 11.8.9(b). After unwrapping along the time-axis, the continuous phase profile depicted in Figure 11.8.9(c) is obtained. Subsequently the frequency of vibration can be calculated from the time shift of the maxima; in this case it is evaluated as 5.68 Hz. The amplitude of phase change at this point $A_\Phi$ is known after unwrapping, from which the surface height at this point can be calculated.

**Figure 11.8.9.** (a) Grey value variation at a discrete point in the [Tay, et al., 2004] experiment. (b) Wrapped phase value at this point. (c) Continuous-phase profile after unwrapping.

Often it can be observed that the maximum and minimum values of each cycle of phase variation ($2\pi$ change) are slightly different. This is due to fluctuation of the LCD panel and intensity of the projector light source. Relatively large errors in the phase profile also occur when the grey value approaches the extreme values. The errors are introduced by: 1) the maximum or minimum values detected by the camera are slightly different from the actual extreme grey scale values; (2) for a sine-wave configuration, a slight difference in grey level near the extreme values causes a large
change in phase value. The errors can be minimised by proper selection of the recording rate and frequency of the carrier fringes such that the number of sampling points is optimised within one cycle of grey level change.

At a certain instant time $T$, a combination of phase values on each pixel produces a wrapped spatial phase map. After unwrapping, the continuous phase map, which represents the surface profile, can be obtained. Using the calibrated coefficient $k$, the phase map can be converted into a 3-D surface profile. Very often some vertical stripes are observed on the phase map, this is due to the errors introduced by the extreme values of grey level mentioned above. In spatial co-ordinate, these errors can be reduced by applying a filtering mask on the phase map. In many commercial systems, a $3 \times 3$ median mask is used.

To verify the accuracy of this technique, a comparison can be made with the fast Fourier transform (FFT) and conventional four-step phase shifting methods [Quan, et al., 2001]. Four fringe patterns with a phase increment of $\pi/2$ are projected onto a stationary test surface using the same experimental setup. For each fringe pattern, an averaged image can be obtained from numerous images. Four of such images are subsequently used in the four-step phase shifting algorithm, while one of the images is used for the FFT method. As the phase evaluation is carried out point-by-point along the time-axis, the phase scanning method is best suited to determination of a surface with a complicated profile. The maximum difference of the phase value between both methods is small. In the [Tay, et al., 2004] experiment surface height differences of 0.01 mm could be resolved.

It is worth noting that the fringe projection technique is limited to out-of-plane displacement from a reference, and high quality sinusoidal fringes are required to identify the maximum and minimum grey values. The recording rate of the camera should also be higher than the frequency of surface deformation. A recording rate of at least eight times of the temporal change of the surface deformation frequency is found adequate.

Some concluding remarks

The fringe projection technique requires besides the large and expensive experimental set-up a lot of computational effort. A critical issue using this technique is to extract the phase signal from a number of phase shifted fringe patterns.

The phase angle obtained is wrapped by a factor of $2\pi$ and can be unwrapped by different phase unwrapping algorithms [Strand and Taxt, 1999] or [Ghiiglia and Pritt, 1998]. However, the problem of path dependence, due to the existence of residues in a wrapped phase map, is often encountered during the phase unwrapping process. This means by following different unwrapping paths, an algorithm would produce different results. Several methods have been reported to eliminate the influence of residues. A block path algorithm proposed by [Goldstein, et al., 1988] connects positive residues and negative residues by “branch cuts”. By following a path without crossing any branch cut, it is able to produce a unique unwrapped phase map and hence the phase unwrapping process would be path independent. The algorithm connects a residue with its nearest opposite charge neighbour based on a least length principle. Although this strategy is effective in generating short branch cuts, it does not take into consideration of the quality of phase data. A high-quality phase area may be separated into discrete regions, which would result in discontinuities in a surface profile. An alternative method is the quality-guided phase unwrapping algorithm, which uses a quality map to guide the unwrapping process instead of directly eliminating residues. Since the algorithm is an integration process, in which the unwrapped phase value of a pixel is dependent on the phase values of pixels that have been unwrapped, an accurate quality map would lead reliable phase data to be unwrapped at an early stage and hence unwrapping errors would be confined to a minimum area. [Bone, 1991] first incorporated
phase quality into phase unwrapping by means of a quality mask. This was followed by the work of [Quiroga, *et al.*, 1995], [Lim, *et al.*, 1995] where quality-guided algorithm is developed from “a quality mask” to an adaptive algorithm without the need of a threshold.

A quality map consists of arrays of values that define the quality or goodness of each pixel in a phase map. Depending on applications, various quality maps can be generated. Some quality maps are derived from a wrapped phase map; while others are extracted directly from the data where wrapped phase is derived, such as the fringe contrast map. Regardless of how a quality map is derived, the algorithm that uses the quality map to guide phase unwrapping is similar. A detailed quality-guided phase unwrapping algorithm can be found in [Ghiglia and Pritt, 1998] and the fringe contrast based phase unwrapping algorithm is a type of quality guided phase unwrapping algorithm. The fringe contrast based algorithm unwraps high contrast phase at an early stage and low contrast phase at a later stage so that low contrast data do not affect high contrast data. The algorithm does not consider the influence of residues. Instead, it is based on the assumption that an accurate fringe contrast map would guide an unwrapping path without encircling any unbalanced residues. A detailed description can be found in [Chen, *et al.*, 2005].

Currently no liquid metal experiment to the knowledge of the author has been performed using this technique, but the results obtained for nearly reflecting moving surfaces shows encouraging results. Moreover, the recent progress in the image processing techniques triggered by the particle image velocimetry (PIV) as well as the use of this technique in the car manufacturing industry in combination with the rapidly increasing computing power offers the potential feasibility in the near future for the application in liquid metal systems.

11.8.1.3.2 Laser speckle interferometry

If a laser beam illuminates a continual deformation of a surface, it will lead to a temporal speckle pattern on the observation plane. Recording this time-dependent speckle pattern the deformation of the surface of an object can be obtained. In general two methods, the scanning phase method (SPM) and the time sequence phase method (TSPM), are used for measuring the displacement caused by the deformation in temporal speckle pattern interferometry (TSPI). Their principle is that by capturing a series of speckle interference patterns related to the object deformations, the fluctuations in the intensity of the interference patterns can be obtained. Through scanning these fluctuations and estimating both the average intensity and modulation of the temporal speckle interference patterns, the phase maps for whole-field displacements are calculated. In this way one is capable of quantitatively measuring continual displacements simply using a conventional electronic speckle pattern interferometry (ESPI) system without phase shifting or a carrier. The elaboration on the new methods is given in the paper by [Li, *et al.*, 2001] or [Toh, *et al.*, 2001].

The data reduction of the acquired images and the subsequent image processing is similar to that of the fringe projection. The speckle interferometry also requires a significant mathematical and computational effort. Due to the use of a more sophisticated optical system compared to the fringe projection the image processing is more time consuming. However, the attainable spatial resolutions using speckle interferometry is an order of magnitude larger than that of the fringe projection. The principle set-up of the speckle interferometer is shown in Figure 11.8.10.

The phase map of a displacement field caused by the deformation of the surface can be evaluated directly with temporal series of speckle patterns captured by a conventional ESPI system or a speckle interferometry system. This is a real-time shifting or time-carrier method, where the phase change is caused by the continuous deformations of the tested surface. It is significant to simplify the
measurement system, so as to be suitable to an execrable environment. Comparing with the Fourier transform method, SPM and TSPM simply needs fewer frames to evaluate the phase map. In the lower limitation, only one period including six frames is necessary to evaluate the phase data. This means that the displacement down to half of a wavelength of the illumination beam still can be resolved. The upper limitation of the measurement highly depends on the correlation of the temporal speckle patterns and the storage ability of a computer system. However, the total displacement measured by the speckle interferometry methods is much greater than by the ESPI with the same testing system.

11.8.2 Acoustic distance measurements

Generally, two possibilities to acquire the surface shape of a wavy liquid metal surface are possible. The first is to install the ultrasound sensor in the gas phase and transport the sound waves through the gas. This technique requires first a gas filling as transport medium and a detailed knowledge of the temperature layering within the gas, which determines the sound velocity; but, it has the advantage of the temperature decoupling of the sensor from the liquid and moreover, the wetting problem as well as the corrosion of the sensor is avoided. However, in most problems the free liquid metal surface is shaped by the pressure field and the velocity distribution within the flow. Hence, for a detailed analysis of the problem at least two quantities must be known. Applying, an ultrasound sensor directly in the fluid gives the opportunity to capture the velocity field and the surface height, but faces the above named problems. The subsequent paragraphs first describe the surface shape measurement using an ultra-sonic system operating through air and the second one a system, which acquires both velocity and surface position using a sensor being in direct contact with the liquid metal.

11.8.2.1 Ultrasonic distance measurement using frequency shift-keyed signal

The techniques of distance measurement using ultrasound in air or noble gases include the time-of-flight (TOF) technique (see e.g. [Parilla, et al., 1991], [Marioli, 1992], [Tardajos, et al., 1994]), single-frequency continuous wave phase shift [Young and Lee, 1992], two-frequency continuous wave method (e.g. [Shoenwald and Smith, 1984]), combining methods of TOF and phase-shift (e.g. [Gueuning, et al., 1997]), multi-frequency continuous wave phase shifts (e.g. [Kimura, et al., 1995] or [Huang, et al., 1999]) and a multi-frequency AM-based ultrasonic system [Yang, et al., 1994]. The TOF method has been extensively discussed in the recent literature. The pulse propagates through the transmission medium and is reflected by the surface. The reflection using ultrasound is independent of the optical properties of the fluid compared to the previously discussed optic
techniques. The time taken for the pulse to propagate from transmitter to receiver is proportional to the reflector’s range. The distance between the reflector and transducer site is \( d = (c \cdot t)/2 \), where \( c \) is the sound velocity and \( t \) the TOF. Using TOF to measure the distance, the system errors are primarily due to amplitude degradation of the received signal, and uncertainty in the speed of sound. The method is more efficient when the energy transferred between emission and reception is high, but it is strongly limited by the ultrasonic transducers, which must be of rather high quality factor, high power, and high cost. Increasing the frequency of the pulse transmitted can improve the accuracy and the resolution, but the higher frequency of the pulse transmitted, the greater the attenuation per unit distance. Therefore the maximum measurable distance will also be reduced. Normally, if distances in air of a few meters are to be measured, frequencies in the range 20-100 kHz must be used in order to maintain suitable receiver signal levels [Webster, 1994]. So the TOF method of range measurement is subject to high levels of errors (about 1 cm) when used in an air medium, thus limiting its applications.

In order to obtain accurate distance estimations, a superior system choice is the phase data of a steady-state frequency received signal with reference to its transmitted signal. This is because the distance information is derived from the phase difference of a repeating signal which is sampled for a statistically significant number of wave periods. Thus, the random variations in phase shift (originating from turbulence, environmental noise, electronic noise, etc.) tend to cancel themselves out in an averaging process. Most applications of range measurement in air using ultrasound apply a phase-shift analysis of single-frequency continuous-wave transmission [Figueroa and Barbieri, 1994]. If the transmitter is energised with a continuous sinusoidal signal, the signal corresponding to the received acoustic wave can be written as \( V_r(t) = A_r \sin(\omega_0 t + \theta) \). Here \( A_r \) is the peak value of the received signal, \( \omega_0 \) is the resonant angular frequency of the transducer, and \( \theta \) is the phase shift, which is linearly proportional to the measured surface distance. The range or distance \( L \) can be determined by the phase shift \( \theta \) of a single frequency if the maximum ranging distance does not exceed one full wavelength; otherwise phase ambiguity will occur. Thus the maximum achievable range for transducer with a resonant frequency of 40 kHz is about 4.25 mm which is too short for scientific interests. Although this disadvantage can be improved by a multiple-frequency continuous wave technique, which calculates the surface distance at ranges much greater than one wavelength, the range of measurement is still too short (only 1500 mm) [Huang, et al., 2002].

[Gueuning, et al., 1997] presented an algorithm for the distance measurement which combines both the pulse TOF method and the phase-shift method and can obtain accurate distance measurement better than 1 mm. The technique is based on a particular signal processing method which determines the approximate TOF by computing the cross-correlation between the envelope of the transmitted and received signals. The carrier phase shift between emission and reception is then computed in order to refine the final result. But the accuracy of this computed the phase shift is limited by the amplitude accuracy of the samples and the resolution of the analogue to digital (A/D) converter, and the refined range does not exceed a wavelength of the transmitted signals. [Webster, 1994] presents a method that is based upon the binary frequency shift-keyed (BFSK) signal followed by data acquisition and signal processing of phase-digitised information from the received signal. The method can reduce many of the problems that arise when dealing with the non-ideal behaviour of ultrasonic transducers. But the TOF is estimated by the time at which the transition between the frequency \( f_1 \) and \( f_2 \) occurs and is determined from the phase data, which are easily influenced by noise, and errors arise.

In the newest technological trend combined methods are used to achieve better, more accurate distance measurement. In these distance measurement systems two independent signal part are analysed. One part estimates the TOF, and the other part calculates the phase-shift difference between the transmitted and received signal. This method is based upon the transmission of a BFSKs signal. Upon reception of the pulse, the TOF is computed by the time at which the change between each discrete frequency occurs and two phase shifts between the transmission and reception signals are detected in
order to enhance the accuracy of the time measurement. The phase shifts are computed by a counter

technique to avoid the limitation caused by the amplitude of the signal and the finite bits of the A/D

c converter.

Operation principle

The principle of the distance measurement system is similar to the operation of using a ruler. At

first a coarse measurement is done, and then a fine measurement is adopted to refine the final

result. Thus the high accuracy is achieved.

The transmitted signals and the received signals are shown in Figure 11.8.11. The \( S_T \) is the

transmission signal of a BFSK, which has two frequencies \( f_1 \) and \( f_2 \) depicted in Figure 11.8.11(a). The \( T_r \) is the period of \( S_T \). The \( S_R \) is the received signals corresponding to the transmitted signals as

illustrated in Figure 11.8.11(b).

Figure 11.8.11. UDV signal emission for surface distance measurement.

(a) Transmitted signals and (b) received signals.

There are two steps to processing of the received signal. The elapsed time \( \Delta t \) (TOF), which is the

round-trip travel time of the transmitted signal from the transmitter to the reflective target (surface)

and back to the receiver, can be calculated by received/transmitted signals and written as \( \Delta t = t_2 - t_1 \).

Here, \( t_1 \) is the time when \( f_1 \) changes to \( f_2 \) of the transmitted signal, \( t_2 \) is the time when \( f_1 \) changes to \( f_2 \) of

the received signals corresponding to the transmitted signals. The distance of the emitter to the surface

can be expressed as \( d = \frac{c \Delta t}{2} \), where \( c \) is the sound velocity.

The detection of the phase shift is based on the two-frequency continuous wave method of

ultrasonic distance measurement. The phase shift of \( \theta_1 \) and \( \theta_2 \) can be detected by the received signals

corresponding to the transmit signals. A continuous wave with frequency \( f_1 \), and a received signal

(\( SR \)) with frequency \( f_1 \) and \( f_2 \) are shown in Figure 11.8.12. The phase shift \( \theta_1 \) is the difference in

phase between the continuous wave and the received signal at \( f_1 \). The phase \( \theta_1 \) can be written as

\( \theta_1 = \frac{2\pi(t_2 - t_1)}{T_1} \), where \( T_1 \) is the period of the received signal of \( f_1 \). Similarly, the phase \( \theta_2 \) is the

difference in phases regarding the received signal at \( f_2 \). A comparison of the two phase shifts allows

calculating the distance. The formulas can be written as:

\[
\begin{align*}
L &= \frac{1}{2} \left( n_1 + \frac{\theta_1}{2\pi} \right) \lambda_1 \\
L &= \frac{1}{2} \left( n_2 + \frac{\theta_2}{2\pi} \right) \lambda_2
\end{align*}
\] (11.125)
where \( L \) is the distance between the surface point and transducer site, \( \lambda_1, \lambda_2 \) are the wavelengths of the ultrasound, \( n_1, n_2 \) are integers, and \( \theta_1, \theta_2 \) are phase shifts. Due to the different wavelengths, the expression for the difference of the phase shift may be derived from Eq. (11.125) in the way:

\[
\Delta \theta = \pi \cdot L \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) \tag{11.126}
\]

The integers \( n_1 \) and \( n_2 \) in Eq. (11.125) have only two possible values: \( n_1 = n_2 \) and \( n_2 = n_1 + 1 \). So the difference of the phase shifts can be defined by the following algorithm:

If \( \theta_2 > \theta_1 \), then \( \Delta \theta = \theta_2 - \theta_1 \) and

If \( \theta_2 < \theta_1 \), then \( \Delta \theta = \theta_2 - \theta_1 + \pi \tag{11.127} \)

If the velocity of ultrasound along the signal path is constant, say \( c \), the wavelength \( \lambda \) can be determined as: \( \lambda_1 = cf_1 \), \( \lambda_2 = cf_2 \). Here, \( f_1 \) and \( f_2 \) are the frequencies of the ultrasonic wave. From Eq. (8.19) the distance of the surface can be expressed as:

\[
L = \frac{\Delta \theta \cdot c}{\pi \Delta f} \text{ with } \Delta f = f_2 - f_1 \tag{11.128}
\]

The distance to the surface \( L \) can be uniquely determined by the difference of the phase shifts \( \Delta \theta \), if the maximum distance does not exceed the half of wavelength of \( \Delta f \). Otherwise a phase ambiguity will occur. The maximum achievable detecting range with Eq. (8.18)a is about 4.375 mm and with Eq. (11.128) is about 175 mm (taking \( c = 350 \text{ m/s}, f_1 = 40 \text{ kHz}, f_2 = 41 \text{ kHz} \)).

**Figure 11.8.12. Illustration of the of the two phase shifts \( \theta_1 \) and \( \theta_2 \)**

In order to obtain a high accuracy over a large distance \( d \) the following algorithm can be used. The distance \( d \) can be obtained by \( d = (c \Delta t)/2 \), where the \( \Delta t \) is TOF. \( d \) is divided into regions \([ (k - 1)Lr, kLr] \) \( k = 1,2,3,... \) a schematically depicted in Figure (8.14)a. The \( Lr \) is the wavelength of \( \Delta f \). The distance \( d \) can be expressed as:

\[
d = \frac{1}{2} \left[ (k - 1) + \left( \frac{\Delta \theta}{2\pi} \right) \right] \cdot \frac{c}{\Delta f} \text{ again with } \Delta f = f_2 - f_1 \tag{11.129}
\]
where $k$ is an integer. The region defined by $[(k-1)Lr, kLr]$ is referred to as the number $k$ region. The $k-1$ integer can be obtained by $\text{Int}(\Delta t \Delta f)$ with $\text{Int}[]$ the integer operation. So the estimate of target distance can be expressed by the following algorithm:

$$d = \frac{1}{2} \left[ \text{Int}(\Delta t \Delta f) + \left( \frac{\Delta \theta}{2\pi} \right) \right] \cdot \frac{c}{\Delta f}$$ (11.130)

In order to increase the accuracy, the number $k$ region can be divided by $l$, where $l = \lambda_1 = cf_1$. This is graphically shown in Figure (11.8.14)b. The fine scale measurement of $(\Delta \theta/2\pi)(c/\Delta f)$ can be replaced as $(m + \theta_1/2\pi)c/f_1$, where the integer $m$ can be obtained by $\text{Int}[(\Delta \theta/2\pi)(f_1/\Delta f)]$. The final estimate of distance can be expressed as:

$$d = \frac{1}{2} \text{Int}(\Delta t \Delta f) \cdot \frac{c}{\Delta f} + \frac{1}{2} \left[ \text{Int} \left( \frac{\Delta \theta}{2\pi} \cdot \frac{f_1}{\Delta f} \right) + \frac{\theta_1}{2\pi} \right] \cdot \frac{c}{f_1}$$ (11.131)

Figure 11.8.14. (a) Relation between $d = ct$ and $d = (k-1)Lr + (\Delta \theta/2\pi)Lr$. b.) Relation between $d$, $Lr$ and $l$.

System set-up and operation

The measurement hardware consists of two acoustic transducers with matching exponential horns, a signal generation system, power amplifier, preamplifier and gain-controlled system, frequencies detected system, digital phase meter, and calibration system. A microprocessor-based controller governs the operation of the entire system, more details may be taken from [Huang, et al., 2002]. Before starting the distance measurement the system must be calibrated with a known distance. By choosing appropriate frequencies accuracies in the range of tenth of a millimetre can be obtained with standard variations being in the micrometer range. The temporal resolution is in the range of the UDV systems for velocity measurements in the range of 20-30 Hz. One of the biggest disadvantages affecting the measurement accuracy considerably is that the temperature distribution in the gas environment transporting the sound must be known before starting the surface measurement campaign.

11.8.2.2 Ultrasonic velocity profile meter

The liquid-phase velocity profile below interfacial waves in horizontally-stratified gas-liquid two-phase flows affects the interfacial exchanges of mass, momentum and heat and the growth of the interfacial waves. For cases of practical importance, such as stratified wavy two-phase flows, it is
generally difficult to predict theoretically or measure experimentally the liquid phase velocity profile which is coupled with the wavy interface profile. The theoretical velocity profile with the wavy interface profile is available only for limited cases, such as infinitesimal and solitary waves. Furthermore, both the velocity and interface profiles of the interfacial waves of wavy flows usually deviate greatly from such theoretical profiles.

The ultrasonic velocity profile (UVP) meter, see [Takeda, et al., 1994], [Takeda, 1995] or Section 11.4.1) was developed to measure an instantaneous velocity profile of liquid flows dynamically, using the Doppler shift frequency in echoes reflected at small particles flowing with liquid. The UVP meter combined two methods used in medical; a pulse method to detect the distribution of various tissues from the time delay of reflected pulses and a Doppler method to detect the velocity variation within the fluid using echoes from continuous ultrasound. The transducer emits an ultrasonic pulse, receives reflected echoes until the next pulse emission. Velocity profiles composed of two sets of information – instantaneous velocities at different locations – along the path of ultrasonic pulses, are successively obtained with a short time interval. The particle location is obtained from the time duration between the pulse emission and the echo detection. The applicability of the UVP has been demonstrated for duct flows in various configurations, see Section 11.4.1.

The fact that ultrasound totally reflects at the gas-liquid interface at any incident angles provides a simple technique to detect the liquid gas-interface. If both quantities are required simultaneously lots of precautions and countermeasures have to be taken that multiple reflections from the interface, especially if it is wavy, does not influence the velocity reading. Nevertheless, numerous possibilities to avoid multiple reflections are available and described in the paper by [Nakamura, et al., 1995].

11.9 Summary and final comments

The instrumentation development for special liquid metal adapted technique has increased its speed in the past decade significantly. This observation can be seen from the attached literature list and it is triggered by many aspects, which arises from the nuclear technology both in fission (fast breeder, accelerator-driven systems to transmute nuclear waste or high power density systems) and in fusion (liquid metal cooled blankets or divertors) but also in conventional engineering as steel or aluminium casting, metal refinery or crystal growth for the computer technology. In all of these fields liquid metal adapted instrumentation is required to control the process, ensure the safety and reliability of the individual facility.

The realisation of different nuclear and industrial facilities operating with liquid metals pushed the speed of innovation, since increasing energy costs enforces the demand of a simultaneously economic operation and safe operation.

Of course, the author of this chapter can not cover the whole development process currently underway. This chapter is restricted to the description of the techniques and methods known from the literature or tested by colleagues or by myself. In some cases measurement techniques are described, which were up to now not tested for liquid metals, but show from their principle the feasibility of an application to it. I tried to explain the measurement principle, to describe the algorithms to reduce the measurement data and to sketch the experimental effort to obtain the required quantities property adequately. Of course, many of the techniques described in this context reveal numerous error sources or require model assumptions. I tried to quantify the potential error sources and methodologies to avoid systematic errors. Regarding the model assumptions in some cases necessary to interpret the measured raw data I hopefully mentioned the main ideas completely to the gracious reader and gave the adequate literature sources.
REFERENCES


Ozarapoglu, V. (1972), PhD Thesis Laval Univ., Quebec, Canada.


Velt, I.D., V.I. Petrushaitis, B.S. Sprjgin, I.V. Krasilnikov, Yu.V. Mikhailov, V.R. Tuleninov (1982), 
*Correlation Technique for Flow Rate Measurement of Electro-conductive Fluids and Two-phase Media and a Device for its Implementation*, Int. Patent No. 30.01.82.


Chapter 12
EXISTING HLM FACILITIES FOR EXPERIMENTAL APPLICATIONS*

12.1 Introduction

The use of the heavy liquid metals (HLM) lead-bismuth eutectic (LBE) and lead (Pb), as cooling medium and spallation material has been envisaged in the field of accelerator-driven systems (ADS), which are devoted to transmute and reduce the radiotoxicity of nuclear waste. An increasing interest on HLM can be identified also in other research and industrial fields, as for instance the energy production with advanced nuclear systems, the hydrogen production with nuclear power and the development of spallation neutron sources for medical applications and materials studies. Therefore, scientific and technological activities focused on materials compatibility, thermal fluid dynamics characterisation and technology issues have been launched. In this frame a large effort has been made to built and operate HLM test facilities in support to the previously mentioned applications. In the following paragraphs the descriptions of the HLM facilities available at the laboratories of the expert groups participating to the realisation of this handbook are given. A list of the facilities is given also in Table 12.1 at the end of this chapter.

The available facilities covers almost all basic studies needed to design HLM nuclear systems working at temperatures up to 550°C. However, further needs can be envisaged for applications at temperature ranges above 600°C and for specific analysis concerning safety aspects in representative conditions (i.e. interaction with secondary coolants, loss of coolant, etc.), specific component testing in prototypical conditions (i.e. dedicated heat exchanger, pump, etc.) and in-service inspection and repair (ISI&R).

In addition the need to characterise and validate for the reactor applications specific measurement techniques (e.g. oxygen sensors) and operational techniques (e.g. pumps, flow meters) in a combined neutron field and HLM environment can be also envisaged.

In the sections that follow the available facilities are listed, and the objectives and the operational parameters are reported. As can be seen, some facilities have been built to provide data for the three fields of investigation previously mentioned.

12.2 Technological facilities and their applications

Technological and liquid metal chemistry, experiments performed in this field are aimed at the development of measurement tools and device to realise and execute thermal-hydraulics benchmark experiments with well known and measurable initial and boundary conditions. Moreover, these facilities are aimed to validate specific procedures for large circuit operation. The relevant measurement tools and devices to be applied for thermal-hydraulics experiments are:

* Chapter lead: Concetta Fazio (FZK, Germany).
heat flux simulation tools;
flow meter devices;
pressure measuring systems;
local velocity measurement systems;
development of tools to measure locally and globally free surfaces.

A second item is the study of liquid metal chemistry, where the development and validation oxygen monitoring and control systems is one of the most important task. Three types of oxygen control methods are currently analysed, which make use of a mixture of hydrogen/moisture; oxygen and hydrogen gases and PbO pellets respectively. Concerning the measurement of the oxygen content in the liquid metal, electrochemical oxygen probes are presently developed. Activities are focused on the definition of a standardised calibration procedure to assess the probes for reliability in conformity to nuclear use. Key variables include dose, dose rate, thermal transients, pressure variations, etc.

Facility: Technologies of heavy liquid metal systems (THESYS) loop – Figure 12.2.1
FZK, Germany

Objectives:
- Optimisation of Karlsruhe OCS for loop applications.
- Development of thermal-hydraulic measurement techniques.
- Heat transfer and turbulence experiments.
- Development of high performance INCONEL heaters (fuel rod simulator).
- Set-up of thermal-hydraulic data base for physical model development and code validation.

Operational parameters:
- Maximum temperature: 550°C.
- Maximum flow rate: 3.5 m³/h.
- LBE volume: 100 l.
- The loop was operated originally with LBE, but it is presently under modification to enable the use of Pb. The relevant of the loop are:

Facility: Karlsruhe Oxygen Control System (KOCOS) – Figure 12.2.2
FZK, Germany

Objectives:
- Development of the Karlsruhe Oxygen Control System OCS.
- Measurement of diffusion coefficients of oxygen in Pb-Bi.
- Measurement of oxygen mass exchange rates.

Facility: Karlsruhe Oxygen Sensor in Molten Alloys (KOSIMA) – Figure 12.2.3
FZK, Germany

Objectives:
- Development of oxygen sensors.
- Optimisation of oxygen sensor performance as for reference system, reproducibility and long-term stability.
- Calibration of oxygen sensors.
Figure 12.2.1. Scheme and photo of THESYS

Figure 12.2.2. Diagrammatic sketch of KOCOS experiment
Facility: Chemistry and Operation (CHEOPE) – Figure 12.2.4

**ENEA, Italy**

The device consists of three different loops:
- CHEOPE I for thermal-hydraulic activities.
- CHEOPE II for liquid metal chemistry studies.
- CHEOPE III for corrosion studies at high oxygen content.

**Objectives:**
- Corrosion investigation in lead alloys at high oxygen content.
- Component test and development.
- Physico-chemistry.
- Thermal-hydraulic experiments: heat transfer characteristics, target development, pumping systems, etc.

**Operational parameters:**
- Maximum temperature (Cheope III): 500°C.
- Maximum flow rate (Cheope III): 1.2 m³/h.
- Volume Cheope I: 900 l.
- Volume Cheope II: 50 l.
- Volume Cheope III: 50 l.
- Oxygen meter: Yes.
- Oxygen control: Yes.
- Heavy liquid metal: Pb-Bi.

Facility: SOLDIF – Figure 12.2.5

**CEA, France**

**Objectives:**
- Determination of solubility and diffusivity of dissolved species in molten lead or lead alloys by means of electrochemical techniques using a molten salt electrolyte.
- Characterisation of the oxide layer on a metallic material immersed in molten lead or lead alloys by means of electrochemical techniques.

**Operational parameters:**
- Maximum temperature: 500°C.
- Maximum flow rate: Static.
- Number of electrochemical cell: One.
- Heavy liquid metal: Pb-Bi or Pb.
Figure 12.2.4. Scheme and photograph of CHEOPE
Figure 12.2.5. Scheme and photograph of SOLDIF
**Facility: Standard Technology Loop for Lead Alloy (STELLA) – Figure 12.2.6**

**CEA, France**

**Objectives:**
- Lead alloys chemistry monitoring and control.
- Oxygen sensors validation.
- Purification process development and qualification.
- Oxygen control process development and qualification based on mass exchange unit (PbO).
- Dip sampling system qualification on loop.

**Operational parameters:**
- Maximum temperature: 550°C.
- Temperature gradient: 150°C max.
- Volume: 32 litres.
- Max flow rate: 1 m³/h at 3 m NPSH.
- Number of test sections: 1.
- Oxygen control system (OCS): Yes.
- Heavy liquid metal: Pb-Bi.
- Corrosion protection: Aluminisation by pack cementation.

**Facility: Vacuum Interface Compatibility Experiment (VICE)**

**SCK•CEN, Belgium**

**Objectives:**
- Study of gas transport in the proton beam line and possible compound formation in a realistic 1-1 pumping geometry mock-up.
- Detailed investigation of initial and long-term out-gassing of Pb-Bi including component identification.
- Study of metal evaporation.
- Simulation of emanation behaviour of volatile spallation products.

**Operational parameters:**
- Beam-line geometry (5 m).
- Maximum temperature: 500°C.
- Minimum operating pressure: $10^{-7}$ mbar – UHV technique.
- Heavy liquid metal: Pb-Bi.
- Useful Pb-load: 100 kg.
- Vacuum pressure controller: $10^{-7}$ mbar – 1 bar.
- High resolution rest gas analyser.
- Gas flow rate differential calibration system.
- Magneto-hydrodynamic stirring.
- Plasma cleaning system (10 kW).
Figure 12.2.6. Scheme and photograph of STELLA
**Facility: Pre-conditioning Vessel (PCV) – Figure 12.2.7**

SCK•CEN, Belgium

**Objectives:**
- Investigation of conditioning and cleaning procedures of Pb-Bi eutectic to a suitable level for use in a windowless spallation target loop.
- Outgassing studies of Pb-Bi eutectic (stage 1).

**Operational parameters:**
- Maximum temperature: 500°C.
- Maximum pressure: 10 bar.
- Minimum operating pressure: 10⁻⁷ mbar – UHV technique.
- Heavy liquid metal: Pb-Bi.
- Useful Pb-load: 100 kg.
- Oxygen control system: H₂/H₂O gas.
- Plasma cleaning system: 10 kW.
- Rest gas analyser: Hi-tech quadrupole.
- Magneto-hydrodynamic stirring.

**Facility: Target Complex 1 (TC-1) – Figure 12.2.8**

University of Nevada, Las Vegas, USA

**Objectives:**
- Demonstrate long-term, sustained operation of MHD pump for LBE loop.
- Complete prototype evaluation for TC-1 complex on behalf of ISTC partners.
- Train students in the operation of molten metal engineering scale systems.
- Examine long-term performance of target systems under non-irradiation conditions.

**Operational parameters:**
- Maximum temperature: TBD (not to exceed 300°C at pump inlet).
- Minimum temperature: 200°C.
- Maximum (typical) flow rate: 15 (TBD) m³/hr.
- Electrical power: TBD (70 kW max.).
- Number of test sections: 0.
- Number of samples: 0.
- Oxygen control system (OCS): None.
- Oxygen sensors: None.
- Heavy liquid metal: Pb-Bi.

---

*Figure 12.2.7. Photograph of inside PCV*
Figure 12.2.8. Schematic/components arrangement of TC-1
Facility: Steam Injection and Oxygen Concentration Control Apparatus – Figure 12.2.9

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Japan

Objectives:
- Performance of oxygen sensor.
- Control of oxygen potentials in Pb-Bi.
- Material corrosion and corrosion product in Pb-Bi.
- Carry-over of Pb-Bi mist and impurities into steam flow.
- Dissolved H₂ in steam and water.
- Chemistry and transport of metal elements in Pb-Bi.

Operational parameters:
- Maximum temperature: 500°C.
- Maximum pressure: 0.5 MPa.
- Pb-Bi inventory: 70 kg.
- Water/steam inventory: 30 kg.
- Maximum water/steam flow rate: 25 g/min., 250°C.
- Pb-Bi flow system: Steam gas lift pump.
- Maximum electrical power Pb-Bi: 6 KW.
  Maximum electrical power water/steam: 4 KW.
- Pb-Bi test vessel number: 1.
  Size: φ260 × 760 mm.
  Material: Cr-Mo steel.
- Maximum apparatus height: 3.2 m.
- Oxygen control system (OCS): Yes (hydrogen-dissolved water).
- Heavy liquid metal: Pb-Bi eutectic.
Figure 12.2.9. Flow diagram and photo of the Steam Injection and Oxygen Concentration Control Apparatus
12.3 Materials testing facilities and their applications

Materials testing, the facilities used to characterise the materials behaviour in the liquid metal are principally of two types. One are static tests facilities, which are used for materials screening tests and for basic corrosion mechanism investigations. Usually on these static devices an oxygen control and monitoring system is installed in order to evaluate the basic corrosion mechanism in well controlled oxygen conditions. Some of these static devices are also devoted to the mechanical testing of non-irradiated and irradiated materials in the liquid metal. The second type of materials testing facilities are loops. The tests performed with the loops are of importance for the evaluation of the long-term corrosion resistance of the materials. The tests were typically performed under well known conditions in terms of oxygen concentration, temperature, HLM flow rate. The database produced with the loop tests can be employed for the development and validation of corrosion prediction models.

**Facility: Corrosion Test Stand for Stagnant Liquid Lead Alloys (COSTA) – Figure 12.3.1**

FZK, Germany

*Objectives:*

- Investigation of corrosion mechanisms.
- Influence of protection layers and coatings on corrosion.
- Investigation of GESA treated surfaces.
- Influence of surface alloying on corrosion.

**Facility: Corrosion in Dynamic Alloys (CORRIDA) – Figure 12.3.2**

FZK, Germany

*Objectives:*

- Long-term corrosion investigations of structural materials in flowing LBE.
- Long-term corrosion investigations of coated materials in flowing LBE.
- Investigations on the mechanisms and the kinetics of material/LBE interactions.
- Modelling of corrosion/precipitation behaviour in LBE.
- Investigations on the applicability of “Oxygen Control System (OCS)” in large LBE loops.
- Testing of appropriate zirconia-based oxygen sensors in LBE as part of the OCS.

*Operational parameters:*

- Maximum temperature: 550°C.
- Minimum temperature: 400°C.
- Maximum (typical) flow rate: 4 (2) m/s.
- Electrical power: 170 kW.
- Number of test sections: 2.
- Number of samples: Ca. 32.
- Oxygen control system (OCS): Via H₂/H₂O ratio in gas phase.
- Oxygen sensors: 3 in LBE, 1 in gas phase.
- Heavy liquid metal: PbBi.
Figure 12.3.1. Sketch and photo of the COSTA facility
Figure 12.3.2. Scheme and photo of CORRIDA

[Diagram of CORRIDA system with labeled components such as Oxygencontrol box, Air cooler, Flowmeter, Magnetic trap, and Dump tank.]

[Photo showing the actual setup of CORRIDA with pipes and machinery.]
Facility: Lead Corrosion (LECOR) – Figure 12.3.3

ENEA, Italy

Objectives:
- Corrosion investigation in lead alloys.
- Component test and development.
- Physico-chemistry.

Operational parameters:
- Maximum temperature hot leg: 500°C.
- Maximum flow rate: 4.5 m³/h.
- Maximum electrical power: 4 MW.
- Number of test sections: 3.
- Oxygen meter: Yes.
- Oxygen control: Separate addition of hydrogen and oxygen.
- Heavy liquid metal: Pb-Bi.

Facility: Development of Lead-alloy Technology and Applications (DELTA) – Figure 12.3.4

LANL, USA

Objectives:
- Corrosion tests of structural and surface treated materials in flowing LBE.
- Investigations on mechanisms of material/LBE interactions.
- Investigations and benchmarking of corrosion/precipitation and system kinetics models.
- Implementation, testing and improvement oxygen sensors and control systems in large LBE loops.
- Thermal hydraulics experiments (e.g. natural convection) and system modelling (e.g. TRAC) and benchmarking.
- Development and testing of components, data acquisition and control systems.

Operational parameters:
- Maximum temperature: 550°C.
- Minimum temperature: 400°C.
- Maximum (typical) flow rate: 5 (2) m/s.
- Electrical power: 65 kW (main heater).
- Number of test sections: 2 (corrosion, scc).
- Number of samples: 186 (in 32/holder batches).
- Oxygen control system (OCS): Direct injection of O₂/He and H₂/He.
- Oxygen sensors: 4 in LBE, 1 in gas phase.
- Heavy liquid metal: Pb-Bi.
Figure 12.3.3. Scheme and photo of LECOR

Flow-rate = 1.2 l/s
Max. Temp. = 550°C
Pressure = 400 kPa
Figure 12.3.4. Scheme and photo of DELTA loop
Facility: Lead Correlation Stand (LCS) – Figure 12.3.5

LANL/UNLV, USA

Objectives:
- Transfer and extend LBE coolant technology to high temperature Pb systems.
- Corrosion tests of structural and surface treated materials in flowing Pb.
- Thermal-hydraulics experiments (e.g. natural convection and flow stability).
- Adapting and testing of sensors, components, data acquisition and control systems to in-Pb use at higher temperatures.
- Test ODS steel (MA956) welding and construction for the loop.

Operational parameters:
- Maximum temperature: 700°C.
- Minimum temperature: 400°C.
- Maximum flow rate: 0.25 m/s.
- Electrical power: 15 kW (main heater).
- Number of test sections: 1 (corrosion).
- Number of samples: TBD.
- Oxygen control system (OCS): Direct injection of O₂/He and H₂/He.
- Oxygen sensors: 2.
- Heavy liquid metal: Pb.

Facility: COLIMESTA – Figure 12.3.6

CEA, France

Objectives:
- Corrosion studies of materials (including welds) and coatings.
- Corrosion mechanisms.
- Effect of oxygen content on corrosion processes.
- Corrosion kinetics.
- Development of corrosion models.

Operational parameters:
- Maximum temperature: 500°C.
- Maximum flow rate: Static.
- Number of test sections: 2.
- Oxygen control system (OCS): Yes.
- Heavy liquid metal: Pb-Bi.
- Corrosion protection: Aluminisation by pack cementation max.
Figure 12.3.5. Schematic of the Lead Correlation Stand (LCS)
Figure 12.3.6. Scheme and photo of COLIMESTA
Facility: CICLAD – Figure 12.3.7

CEA, France

Objectives:
- Corrosion studies of materials (including welds) and coatings.
- Effect of hydrodynamic on corrosion by means of a rotating cylinder (especially at high velocity and including erosion phenomena).
- Effect of oxygen content on corrosion processes.
- Corrosion kinetics.
- Development of corrosion models.

Operational parameters:
- Maximum temperature: 500°C.
- Maximum flow rate: 5 m s\(^{-1}\) corresponding to 5000 rev.min\(^{-1}\).
- Number of test sections: One with the rotating specimens, one with in-pipe specimens.
- Oxygen control system (OCS): Yes.
- Heavy liquid metal: Pb-Bi.
- Corrosion protection: Aluminisation by pack cementation max.
- Oxygen control system (OCS): Yes.

Facility: Liquid Solid Reaction (LiSoR) – Figure 12.3.8

PSI, Switzerland

Objectives:
- Investigation of the effect of simultaneous interaction of irradiation, LBE and mechanical stresses with structural materials.

Operational parameters:
- Maximum temperature: 350°C.
- Maximum flow rate: 1 m/s in the test section.
- Maximum electrical power: 30 kW.
- Number of test sections: 1.
- Oxygen control system (OCS): No.
- Heavy liquid metal: Pb-55.5Bi.

Irradiation parameter:
- Beam energy on target: 72 MeV.
- Beam current: Minimum 15 \(\mu\)A, maximum 40 \(\mu\)A.
- Beam profile on target (Gaussian): \(\sigma_x = \sigma_y = 1.6\) mm.
- Beam wobbling max frequency: 14.3 Hz in X, 2.38 Hz in Y (6:1).
- Beam structure: Wobbling horizontal \(x_{\text{max}} = \pm 2.75\) mm, wobbling vertical \(y_{\text{max}} = \pm 7\) mm.
Figure 12.3.7. Scheme and photo of CICLAD
Figure 12.3.8. Scheme and photo of LISOR

1 – LBE tank, 2 – induction pump, 3 – electromagnetic flow meter, 4 – thermostat (4-1 – LBE-DIPHYL heat exchanger, 4-2 – DIPHYL-WATER heat exchanger, 4-3 – oil pump; 4-4 – ventury tube, 4-5 – bypass, 4-6 – oil expansion tank, 4-7 – valves for oil loop filling and draining), 5-12 – automatic valves, 13 – expansion tank, 14 and 15 – inlet and outlet pipe.
**Facility: Corrosion and Wetting Investigation (CorrWett) – Figure 12.3.9**

**PSI, Switzerland**

**Objectives:**
- Corrosion.
- Thermal cycling.
- Investigation of stressed coated specimens.

**Operational parameters:**
- Maximum temperature: 350°C.
- Maximum flow rate: 0.8 m/s in the test section.
- Maximum electrical power: 8.6 kW.
- Number of test sections: 1.
- Oxygen control system (OCS): No.
- Heavy liquid metal: Pb-55.5Bi.

---

**Facility: SSRT/stagnant experimental set-up – Figure 12.3.10**

**SCK•CEN, Belgium**

**Objectives:**
- Effects of Pb-Bi on the mechanical properties of the structural materials.
- Mutual effect of Pb-Bi and irradiation (mechanical tests on pre irradiated materials).
- Oxygen control and measurements of the dissolved oxygen concentration.

**Operational parameters:**
- Maximum temperature: 500°C.
- Maximum electrical power: 3.5 KW.
- Number of test sections: 1 (autoclave).
- Volume of the liquid metal: ~2.5 litre.
- Oxygen control system (OCS): Yes.
- Heavy liquid metal: Pb-Bi
Figure 12.3.9. Scheme and photo of CorrWett
Figure 12.3.10. Scheme and photo of SSRT/stagnant experimental set-up
**Facility: FELIX/FEDE – Figure 12.3.11**

CIEMAT, Spain

**Objectives:**
- Materials screening test in stagnant conditions.

**Operational parameters:**
- Different gas atmospheres are used.
- Oxygen content is measured.
- Maximum temperature 600°C.

**Facility: CIRCO (natural convection loop) – Figure 12.3.12**

CIEMAT, Spain

**Objectives:**
- Long-term corrosion experiments in quasi-static LBE.
- Testing of oxygen sensors.
- Destructive examination of the loop after the test.

**Operational parameters:**
- Structural material: AISI316L.
- LBE inventory: 1 L.
- Max temperature: 550°C.
- Temperature gradient: 150°C.

**Facility: LINCE (forced convection loop) – Figure 12.3.13**

CIEMAT, Spain

**Objectives:**
- Long-term corrosion experiments in LBE.
- Oxygen control systems in flowing LBE.

**Operational parameters:**
- Maximum temperature: 500°C.
- Maximum flow rate: 2.5 m³/h.
- Number of test sections: 2.
- Lead-bismuth inventory: 170 L.
- Electrical power: 80 kW.
- Oxygen control system installed.
Figure 12.3.11. Scheme and photo of FEDE and FELIX

Figure 12.3.12. Photo of CIRCO
Figure 12.3.13. Scheme of LINCE
**Facility: JAERI Lead-bismuth Static Corrosion Facility (JLBS) – Figure 12.3.14**

JAERI, Japan

**Objectives:**
- Corrosion of materials for ADS components under static condition.
- Screening tests of materials for ADS components.
- Corrosion mechanism of various materials in Pb-Bi.
- Corrosion of surface-treated materials.
- Effect of alloying elements and stress on corrosion in Pb-Bi.
- Effect of impurities in Pb-Bi

**Operational parameters:**
- Maximum temperature: 600°C.
- Number of pots: 4.
- Number of test pieces: 10/pot.
- Diameter of pot: 100 mm.
- Heavy metal weight: 7 kg/pot.
- Oxygen control system (OCS): Yes (partially).
- Heavy liquid metal: Pb-Bi.

**Facility: JAERI Lead-bismuth Flow Loop (JLBL-1) – Figure 12.3.15**

JAERI, Japan

**Objectives:**
- Corrosion study of ADS components in flowing Pb-Bi.
- Development of Pb-Bi flow control.
- Material corrosion-proof test for ADS target test facility at JAERI.

**Operational parameters:**
- Maximum temperature: 450°C.
- Maximum pressure: 5 bar.
- Maximum flow rate: 18 L/min.
- Maximum electrical power: 15 kW heaters.
- Number of test sections: 2.
- Heavy liquid metal: Pb-Bi.

**Facility: CRIEPI Static Corrosion Test Facility – Figure 12.3.16**

CRIEPI, Japan

**Objectives:**
- Behaviour of static corrosion in Pb-Bi

**Operational parameters:**
- Maximum temperature: 700°C.
- Number of pots: 2.
- Number of test piece: 8 / pot.
- Diameter of the pot: 100 mm.
- Step extraction of pieces: Yes.
- Oxygen control system: Yes.
Figure 12.3.14. Photo of JLBS

Figure 12.3.15. Scheme and photo of JLBL-1
Figure 12.3.16. Photo of CRIEPI static corrosion test facility
Facility: KPAL-1 – Figure 12.3.17

KAERI, Korea

Objectives:
- Database for Pb-Bi corrosion.
- Development of oxygen control technique.
- Development of oxygen sensor.
- Development of thermal-hydraulic device for Pb-Bi loop.
- Enhancement of Pb-Bi Loop operation technique.

Operational parameters:
- Maximum temperature: 550°C.
- Maximum flow rate: 3.6 m³/h at 4.0 m NPSH.
- Maximum electrical power: 120 kW.
- Number of test sections: 1.
- Maximum test section height: 0.9 m.
- Oxygen control system (OCS): Yes.
- Heavy liquid metal: Pb-Bi.

Facility: Convectional Loop, COLONRI I – Figure 12.3.18

Nuclear Research Institute Řež, Czech Republic

Objectives:
- Evaluation of corrosion resistance of structural materials in lead-bismuth at different conditions.
- Impact of oxygen content (oxygen technology).

Operational parameters:
- Maximum temperature: 700°C.
- Maximum flow rate: 1-2 cm/s.
- Maximum electrical power: 4 KW.
- Number of test sections: 2.
- Maximum test section height: 2.5 m.
- Oxygen control system (OCS): Yes – indirectly.
- Heavy liquid metal: Pb-Bi.
Figure 12.3.17. KAERI Pb-Bi loop
Figure 12.3.18. Scheme and photo of COLONRI I

Oxidizing mixture generator
Equalizing tank - modification of oxygen content

Gaseous mixture Ar + H2
Demineralised water
Low-temperature part with sample holders
High-temperature part with sample holders

Heating
Filling tank

Oxygen sensor

Direct ion of media flow

V1 V2 V3
### Facility: ANL, USA

**Objectives:**
- Long-term corrosion investigations of structural materials in flowing Pb or LBE.
- Long-term corrosion investigations of coated materials in flowing Pb or LBE.
- Investigations regarding corrosion mechanisms and thermo-mechanical behaviour between materials and Pb or LBE.

**Operational parameters:**
- Maximum temperature: 800°C.
- Minimum temperature: 375°C (LBE), 500°C (Pb).
- Typical flow rate: ~0.01 m/s.
- Electrical power: Low.
- Number of test sections: 2.
- Number of samples: 2.
- Oxygen control system: Via H₂/H₂O ratio in gas phase.
- Oxygen sensors: –.
- Heavy liquid metal: Pb or LBE.

### Facility: H.H. Uhlig Corrosion Laboratory – MIT, US

**Objectives:**
- Corrosion tests of structural and surface treated materials in LBE.
- Investigations on fundamental mechanisms of material/LBE interactions.
- Investigations and benchmarking of corrosion/precipitation and system kinetics models.
- Implementation, testing and improvement oxygen sensors.

**Operational parameters:**
- Maximum temperature: 800°C.
- Minimum temperature: 400°C.
- Maximum/minimum flow velocity: 3/0 m/s.
- Electrical power: 15 kW/test station (heater).
- Number of test stations: 2 (corrosion, scc, rotating electrode).
- Number of samples (immersion): 15/test station (individual crucibles).
- Number of samples (rotating): 1/test station.
- Oxygen control system (OCS): Direct injection of O₂/He and H₂/He, H₂/H₂O.
- Oxygen sensors: 1 in LBE, 1 in gas phase.
- Heavy liquid metal: PbBi/Pb.
Figure 12.3.19. Schematic and photo of quartz convection harp

Figure 12.3.20. Schematic of rotating electrode system and photograph of various components of the system
Facility: Mechanical Properties in Liquid Metals – Figure 12.3.21

University of Lille – UMR CNRS 8517, France

Objectives:
- Determination of mechanical behaviour and mechanical resistance of structural metallic alloys in liquid metals.
  - Monotonic tensile behaviour:
    - standard tensile test (STT) using cylindrical specimen;
    - small punch test (SPT) using 9 mm diameter, 0.5 mm thickness disk.
  - Cyclic behaviour:
    - low cycle fatigue (LCF) on smooth specimen;
    - fatigue crack growth gate (FCGR) on notched specimen.

Operational parameters:
- Maximum temperature: 350°C for LCF, FCGR and SPT, 600°C for STT.
- Maximum flow rate: Static.
- Oxygen control system: No.
- Heavy liquid metals: Pb, Bi, Sn …
- Machine for STT and SPT: 20 kN load capacity strain rate 10^{-2} to 10^{-5} s^{-1}.
- Machine for LCF: 100 kN load capacity – strain control, strain range \( \Delta \varepsilon \): 0.5 \( 10^{-2} \) to 2.5 \( 10^{-2} \) strain rate 10^{-2} to 10^{-4} s^{-1}.
- Machine for FCGR: 100 kN load capacity – load control, four-point bending specimen frequency 15 Hz maxi COD measurement.

Facility: Lead-bismuth Corrosion Test Loop – Figure 12.3.22

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Japan

Objectives:
- Material corrosion in flowing Pb-Bi.
- Oxygen control technique.
- Performance of oxygen sensor.
- Performance of electromagnetic flow meter.
- Performance of ultrasonic flow meter.

Operational parameters:
- Maximum temperature: 550°C.
- Maximum system pressure: 0.4 MPa.
- Maximum flow rate: 0.36 m³/h.
- Maximum electrical power: 22 kW.
- Number of test sections: 1.
- Maximum test section height: 1.5 m.
- Oxygen control system (OCS): Yes (PbO tablets).
- Heavy liquid metal: Pb-Bi eutectic.
- Pb-Bi inventory: 450 kg.
Figure 12.3.21. Photo of fatigue propagation set-up

Figure 12.3.22. Flow diagram and photo of the Lead-bismuth Corrosion Test Loop at TIT
**Facility: Liquid Metal Embrittlement Testing Station 1 (LIMETS1) – Figure 12.3.23**

In operation: August 2004

SCK•CEN, Belgium

Objectives:
- Effects of Pb-Bi on the mechanical properties of the structural materials.
- Calibration of oxygen sensors.
- Effects of oxide layers on the mechanical properties of the structural materials.

Operational parameters:
- Maximum temperature: 500°C.
- Maximum electrical power: 3.5 KW.
- Number of test sections: 1 (autoclave).
- Volume of the liquid metal: ~3.5 litre.
- Oxygen control system (OCS): Yes.
- Heavy liquid metal: Pb-Bi.

**Facility: Liquid Metal Embrittlement Testing Station 2 (LIMETS2) – Figure 12.3.24**

Planned operation: January 2006

SCK•CEN, Belgium

Objectives:
- To test radioactive materials in a controlled lead-bismuth environment.
- Tests that can be carried out are:
  - slow strain rate tests (SSRT);
  - constant load;
  - rising load;
  - crack growth rate (fracture mechanics).

Operational parameters:
- Maximum temperature: 500°C.
- Maximum pressure: 4 Bar.
- Maximum load: 20 kN.
- Displacement rates: $9 \times 10^{-2}$ to $3 \times 10^{-6}$ mm.s$^{-1}$.
- Strain rates (gage length 10 mm): $9 \times 10^{-3}$ to $3 \times 10^{-7}$ s$^{-1}$.
- Maximum displacement: 30 mm.
- Specimens to be tested: Tensile specimen, small size CT.
- Number of autoclaves and loading units: 1.
- Autoclave volume: 3.6 L.
- Autoclave materials: 316L.
- Material conditioning system: 316L.
- Conditioning gasses: Hydrogen, argon.
Figure 12.3.23. Schematic and photo of the LIMETS 1 facility
Figure 12.3.24. Flow sheet of the LIMEST II and photo of instrumentation panel for temperature control of LIMETSII.
12.4 Thermal-hydraulics facilities and their applications

Thermal-hydraulics, the facilities are aimed at the study of basic phenomena as for instance the turbulent heat transfer, the free surface flow and two-phase flows. These phenomena can be studied by performing experiments with simple geometries. In addition, a very challenging activity is the execution of design oriented experiments as for instances experiments devoted to the characterisation of a spallation target or a fuel bundle. The experimental activities are normally prepared with the help of computational analysis (CFD calculations). One of the most important aims of thermal-hydraulics experiments is to improve physical models and to validated the CFD codes. The importance of these activities can be recognised in the fact that CFD codes are regularly used for the layout of the design of an HLM system.

**Facility: Thermal-hydraulics and ADS Design (THEADES) – Figure 12.4.1**

FZK, Germany

**Objectives:**
- Thermal-hydraulic single-effect investigations of ADS components.
- Cooling of the beam window.
- Flow field of a windowless target configuration.
- Cooling of fuel element(s).
- Heat transfer characteristics of a Pb-Bi/Pb-Bi heat exchanger.
- Heat transfer characteristics of a steam generator.
- Heat transfer characteristics of a Pb-Bi/air heat exchanger.
- Set-up of thermal-hydraulic data base for physical model and code validation.

**Operational parameters:**
- Maximum temperature: 450°C.
- Maximum flow rate: 100 m³/h at 4.5 m NPSH.
- Maximum electrical power: 4 MW.
- Number of test sections: 4.
- Maximum test section height: 3.4 m.
- Oxygen control system (OCS): Yes.
- Heavy liquid metal: Pb-Bi.

**Facility: Circolazione Eutettico (CIRCE) – Figure 12.4.2**

ENEA, Italy

**Objectives:**
- Thermal-hydraulic experiments.
- Component development.
- Large scale experiments in pool configuration.
- Liquid metal chemistry in pool configuration.

**Operational parameters:**
- Maximum temperature: 450°C.
- Volume test section: 9480 l.
- Volume storage tank: 9250 l.
- Volume pumping tank: 924 l.
- Oxygen meter: No.
- Oxygen control: Yes (controlling the cover gas).
- Heavy liquid metal: Pb-Bi.
Figure 12.4.1. Scheme and photo of THEADES
Figure 12.4.2. Schematic and photo of CIRCE
Facility: Thermal-hydraulic ADS Lead-bismuth Loop (TALL) – Figure 12.4.3

RIT (KTH), Sweden

Objectives:
- To perform medium-scale heat transfer experiments of TECLA on different heat exchangers.
- Investigation on LBE flow and heat transfer with prototypic thermal-hydraulic conditions (as in conceptual ADS design).
- Thermal-hydraulic characteristics of natural and forced circulation under steady and transient conditions.
- To perform tests representative for accident scenarios and to strengthen the database for code validation in support of EU’s project PDS-XADS.
- Set-up of thermal-hydraulic data base for physical model and code validation.

Operational Parameters:
- Maximum temperature: 500°C.
- Maximum flow rate: 2.5 m³/h.
- Maximum electrical power: 55 kW.
- Electro-magnetic pump: 5.5 kW
- Maximum test section height: 6.8 m.
- Oxygen control system (OCS): No.
- Oxygen control sensors: Yes.
- Heavy liquid metal: Pb-Bi.
- Secondary loop coolant: Glycerol.

Facility: JAERI Lead-bismuth Flow Loop (JLBL-2) – Figure 12.2.4

JAERI, Japan

Objectives:
- Flow study in horizontal Pb-Bi target.
- Proof test of I-target.

Operational parameters:
- Maximum temperature: <450°C.
- Maximum pressure: 2 bar.
- Maximum flow rate: 50 L/min.
- Maximum electrical power: 5 kW heaters.
- Number of test sections: –.
- Oxygen control system (OCS): No.
- Heavy liquid metal: Pb-Bi.
Figure 12.4.3. Schematic and photo of TALL

Figure 12.4.4. Schematic and photo of JLBL-2
**Facility: JAERI Lead-Bismuth flow Loop-3 (JLBL-3) – Figure 12.4.5**

JAERI, Japan

Objectives:
- Thermal fluid test of beam window.
- Proof test of mechanical pump and massive Pb-Bi flow.

Operational parameters:
- Maximum temperature: 450°C
- Maximum pressure: 7 bar.
- Maximum flow rate: 500 L/min.
- Maximum electrical power: 6 kW heaters.
- Number of test sections: 1.
- Oxygen control system (OCS): Yes
- Heavy liquid metal: Pb-Bi.
- Total inventory: 450 litres.

**Facility: Mitsui Engineering and Shipbuilding Test LOOP 2001 (MES-LOOP2001) – Figure 12.4.6**

MES, Japan

Objectives:
- Coolant purification control test.
- Structural materials corrosion test.
- Thermal-hydraulic test.
- Static/transient operation test.

Operational parameters:
- Maximum temperature: 550°C
- Maximum flow rate: 15 L/min
- Maximum electrical power: 6 kW
- Number of test sections: 1.
- Number of test pieces: 1–10.
- Maximum test section height: 1 m.
- Oxygen control system: Yes.
- Heavy liquid metal: Pb-Bi.
Figure 12.4.5. Flow diagram and photo of JBL3 loop
Figure 12.4.6. Scheme and photo of MES
**Facility: CRIEPI Pb-Bi Test Loop on Thermal-hydraulics – Figure 12.4.7**

**CRIEPI, Japan**

**Objectives:**
- Heat transfer characteristics of Pb-Bi.
- Gas lift pump performance in Pb-Bi.
- Flow characteristics of Pb-Bi/gas two phase flow.

**Operational parameters:**
- Maximum temperature: 300°C.
- Maximum pressure: 0.5 MPa.
- Maximum flow rate: 6 m³/h.
- Total electric power supply: 160 KVA.
- Number of heaters and control: 30 (PID controlled).
- Maximum heater power: 5 KVA.
- Diameter of main piping: 2 inches.
- Oxygen control system: No.

**Facility: Wisconsin Tantalus Facility – Figure 12.4.8**

**UW, USA**

**Objectives:**
- Multi-phase flow, heat transfer and flow stability/oscillations of steam/water injection into liquid metal.

**Operational parameters:**
- Maximum temperature: 550°C.
- Minimum temperature: 400°C.
- Maximum (typical) flow rate: 1-10 gram/sec.
- Electrical power: 30 kW.
- Number of test sections: 2 with multiple injectors.
- Heavy liquid metal: Pb and PbBi.
Figure 12.4.7. Schematic and photo of CRIEPI Pb-Bi Test Loop on Thermal-hydraulics

Figure 12.4.8. Schematic and photo of the Wisconsin Tantalus Facility
Facility: Heavy Eutectic Liquid Metal Loop for Investigation of Operability and Safety (HELIOS)  
Figure 12.4.9

Seoul National University (SNU), Korea

Objectives:
- Verification of the natural circulation capability in PEACER-300 (transmutation reactor), corrosion testing and oxygen sensor development.

HELIOS is going to be completed at the end of 2004. Materials corrosion tests are planned for 2005 and the natural circulation tests for 2006.

Design parameters of PEACER-300/HELIOS:
- Reactor thermal power (kW): 850000/60.
- Reactor vessel height (cm): 1400/1000.
- Reactor vessel diameter (cm): 700/5.0.
- Fuel rod active length (cm): 50/50.
- Number of fuel rods: 63433/4.
- Steam generator tube height (cm): 500/500.
- Primary loop pipe inner diameter (cm): 200/5.
- Pb-Bi coolant weight (tonne): –/1.8.
- Total flow (kg/sec): 58,059/10 max.
- Maximum flow speed (cm/sec): 200/200.
- Core exit temperature (C): 400/400.
- Core inlet temperature (C): 300/300.
- Elevation difference between core centre and steam generator centre (m): 8/8.

Facility: Lead-bismuth Water Direct Contact Boiling Two-phase Flow Apparatus – Figure 12.4.10

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Japan

Objectives:
- Operation technique of steam gas lift pump type Pb-Bi-cooled fast reactor.
- Thermal-hydraulics of Pb-Bi-water direct contact boiling flow.

Operational parameters:
- Maximum Pb-Bi temperature: 460°C.
- Steam temperature: 296°C.
- System pressure: 7 MPa.
- Pb-Bi flow rate: 33840 kg/h.
- Steam-water flow rate: 250 kg/h.
- Heater bundle power: 133 kW.
- Number of test sections: 1.
- Length of test section: 7 m.
- Oxygen control system (OCS): Yes (hydrogen-dissolved water).
- Heavy liquid metal: Pb-Bi eutectic.
- Pb-Bi inventory: 1000 kg.
- Water inventory: 50 kg.
Figure 12.4.9. 3-D CAD drawing (a), side-view photograph (b) and design schematic (c) of HELIOS at Seoul National University.
Figure 12.4.10. Flow diagram and photo of the Lead-bismuth-Water Direct Contact Boiling Two-phase Flow Apparatus at TIT.
### Table 12.1. Summary of the international heavy liquid metal test facilities

<table>
<thead>
<tr>
<th>Association/country</th>
<th>Name of the facility</th>
<th>Type of facility</th>
<th>Objectives</th>
<th>OCS – O₂ probe</th>
<th>Tmax</th>
<th>Flow rate</th>
<th>Other information</th>
<th>CP*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Technological facilities</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FZK/D</td>
<td>THESYS</td>
<td>Loop</td>
<td>Development and testing of measurement techniques</td>
<td>H₂/H₂O – yes</td>
<td>550°C</td>
<td>3.5 m³/h</td>
<td>Heated pipe experiment Heated rod experiment</td>
<td>1</td>
</tr>
<tr>
<td>FZK/D</td>
<td>KOKOS</td>
<td>Loop</td>
<td>OCS development</td>
<td>H₂/H₂O – yes</td>
<td>550°C</td>
<td></td>
<td>Diffusion coefficient measurement of oxygen in LBE</td>
<td>3</td>
</tr>
<tr>
<td>FZK/D</td>
<td>KOSIMA</td>
<td>Static</td>
<td>Oxygen sensor development and calibration</td>
<td>H₂/H₂O – yes</td>
<td>–</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>ENEA/I</td>
<td>CHEOPE II</td>
<td>Loop</td>
<td>Liquid metal chemistry</td>
<td></td>
<td>500°C</td>
<td></td>
<td>50 l of LBE</td>
<td>4</td>
</tr>
<tr>
<td>CEA/F</td>
<td>SOLDIF</td>
<td>Static</td>
<td>Solubilities, diffusivities, oxide layer characterisation</td>
<td>? – yes</td>
<td>500°C</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>CEA/F</td>
<td>STELLA</td>
<td>Loop</td>
<td>Oxygen sensor and dip sampling system validation, OCS development</td>
<td>PbO – yes</td>
<td>550°C</td>
<td>1 m³/h</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>SCK•CEN/BEL</td>
<td>PCV</td>
<td>Stirring</td>
<td>Conditioning and cleaning procedures of LBE and LBE outgas studies</td>
<td>H₂/H₂O</td>
<td>500°C</td>
<td></td>
<td>Studies suitable for windowless spallation target</td>
<td>8</td>
</tr>
<tr>
<td>SCK•CEN/BEL</td>
<td>VICE</td>
<td>Stirring</td>
<td>Gas transport in the beam line, outgas, metal evaporation, simulation of spallation products</td>
<td></td>
<td>500°C</td>
<td></td>
<td>Main operating pressure 10⁻⁷ mbar. Studies devoted to the windowless solution.</td>
<td>8</td>
</tr>
<tr>
<td>LANL/USA</td>
<td>DELTA</td>
<td>Loop</td>
<td>Corrosion tests in flowing LBE, corrosion/precipitation and system kinetics models, oxygen sensors and control systems, thermal-hydraulics experiments, components testing, data acquisition and control systems</td>
<td>Yes</td>
<td>550°C</td>
<td>2-5 m/s</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>LANL-UNLV/USA</td>
<td>LCS</td>
<td>Loop</td>
<td>Transfer and extend LBE technology to higher-temperature Pb</td>
<td>Yes</td>
<td>700°C</td>
<td>0.25 m/s</td>
<td>ODS steel (MA956) construction</td>
<td>12</td>
</tr>
<tr>
<td>UNL/USA</td>
<td>TC-1</td>
<td>Target</td>
<td>Long-term sustained operation of MHD pump for LBE loop; examine long-term performance of target systems under non-irradiation</td>
<td>–</td>
<td>TBD (300°C @ pump inlet)</td>
<td>TBD (15 m³/h)</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>JAERI/JP</td>
<td>JLBL-1</td>
<td>Loop</td>
<td>Corrosion studies and development of flow measurement techniques</td>
<td>H₂/H₂O</td>
<td>450°C</td>
<td>18 l/min</td>
<td>Two test sections</td>
<td>14</td>
</tr>
</tbody>
</table>

* CP = contact persons for the facilities. CP are listed at the end of the chapter.
Table 12.1. Summary of the international heavy liquid metal test facilities (cont.)

<table>
<thead>
<tr>
<th>Association/country</th>
<th>Name of the facility</th>
<th>Type of facility</th>
<th>Objectives</th>
<th>OCS – O₂ probe</th>
<th>Tmax</th>
<th>Flow rate</th>
<th>Other information</th>
<th>CP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>MES/JP</td>
<td>MES-LOOP2001</td>
<td>Loop</td>
<td>Coolant purification, thermal-hydraulic and corrosion tests</td>
<td>H₂/H₂O – yes sensor</td>
<td>550°C</td>
<td>15 l/min</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>TIT/JP</td>
<td>Steam Injection and OCC</td>
<td>Apparat.</td>
<td>Oxygen sensor, oxygen potentials in Pb-Bi, Pb-Bi mist and impurities into steam flow, dissolved H₂ in steam and water chemistry and transport of metal elements in Pb-Bi</td>
<td>H₂/H₂O – yes sensor</td>
<td>500°C</td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>FZK/D</td>
<td>COSTA</td>
<td>Static</td>
<td>Corrosion mechanism investigation in controlled conditions</td>
<td>H₂/H₂O – in the gas phase</td>
<td>1000°C</td>
<td>-</td>
<td>200 specimens at 5 different T and 10 different O₂ activities in one run</td>
<td>3</td>
</tr>
<tr>
<td>FZK/D</td>
<td>CORRIDA</td>
<td>Loop</td>
<td>Corrosion rate in controlled atmosphere</td>
<td>H₂/H₂O – yes</td>
<td>550°C</td>
<td>2.4 m/s</td>
<td>Modelling of corrosion precipitation behaviour</td>
<td>2</td>
</tr>
<tr>
<td>ENEA/I</td>
<td>CHEOPE III</td>
<td>Loop</td>
<td>Corrosion at high oxygen content</td>
<td>H₂/O₂ – yes</td>
<td>500°C</td>
<td>1.2 m³/h</td>
<td>50 l of LBE</td>
<td>4</td>
</tr>
<tr>
<td>ENEA/I</td>
<td>LECOR</td>
<td>Loop</td>
<td>Corrosion at low oxygen content, physico-chemistry, component testing</td>
<td>H₂/O₂ – yes</td>
<td>500°C</td>
<td>4.5 m³/h</td>
<td>Three test sections</td>
<td>4</td>
</tr>
<tr>
<td>LANL/USA</td>
<td>DELTA</td>
<td>Loop</td>
<td>Corrosion tests in flowing LBE, corrosion/precipitation and system kinetics models, oxygen sensors and control systems, thermal-hydraulics experiments, components testing, data acquisition and control systems</td>
<td>Yes</td>
<td>550°C</td>
<td>2.5 m/s</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>LANL-UNLV/USA</td>
<td>LCS</td>
<td>Loop</td>
<td>Transfer and extend LBE technology to higher temperature Pb, corrosion tests in flowing Pb</td>
<td>Yes</td>
<td>700°C</td>
<td>0.25 m/s</td>
<td>ODS steel (MA956) construction</td>
<td>12</td>
</tr>
<tr>
<td>CEA/F</td>
<td>COLIMESTA</td>
<td>Static</td>
<td>Effect of oxygen content on the corrosion mechanism</td>
<td>Yes – yes</td>
<td>500°C</td>
<td>-</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>CEA/F</td>
<td>CICLAD</td>
<td>Rotating cylinder</td>
<td>Hydrodynamic effect on corrosion rate</td>
<td>H₂/H₂O – yes</td>
<td>500°C</td>
<td>5 m/s</td>
<td>Development of corrosion mechanism</td>
<td>5</td>
</tr>
<tr>
<td>PSI/CH</td>
<td>LISOR</td>
<td>Loop</td>
<td>“Stress” corrosion under irradiation</td>
<td>No</td>
<td>350°C</td>
<td>1 m/s</td>
<td>Proton beam: 72 MeV, 15-40 μA</td>
<td>7</td>
</tr>
<tr>
<td>PSI/CH</td>
<td>CorWett</td>
<td>Loop</td>
<td>Corrosion, thermal cycling</td>
<td>No</td>
<td>350°C</td>
<td>0.8 m/s</td>
<td></td>
<td>7</td>
</tr>
</tbody>
</table>

* CP = contact persons for the facilities. CP are listed at the end of the chapter.
Table 12.1. Summary of the international heavy liquid metal test facilities (cont.)

<table>
<thead>
<tr>
<th>Association/country</th>
<th>Name of the facility</th>
<th>Type of facility</th>
<th>Objectives</th>
<th>OCS – O₂ probe</th>
<th>Tmax</th>
<th>Flow rate</th>
<th>Other information</th>
<th>CP</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCK•CEN/BE</td>
<td>SSRT/ stagnant</td>
<td>Static</td>
<td>LBE and irradiation on mechanical properties of structural materials, studies on OCS and O₂ measurement</td>
<td>Yes</td>
<td>500°C</td>
<td>–</td>
<td>One test section in autocave with 2.5 l of LBE</td>
<td>9</td>
</tr>
<tr>
<td>CIEMAT/ES</td>
<td>FEDE</td>
<td>Static</td>
<td>Materials testing in controlled conditions and O₂ measurement</td>
<td>Yes</td>
<td>600°C</td>
<td>–</td>
<td>Different gas atmospheres and different O₂ activities, multi-specimen device</td>
<td>10</td>
</tr>
<tr>
<td>CIEMAT/ES</td>
<td>FELIX</td>
<td>Static</td>
<td>Materials testing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>CIEMAT/ES</td>
<td>CIRCO</td>
<td>Loop</td>
<td>Long-term corrosion experiments and oxygen sensor testing</td>
<td>Yes</td>
<td>550°C</td>
<td>2.5 m³/h</td>
<td>Analysis of corrosion products deposition could be performed by destructive examination of the loop</td>
<td>10</td>
</tr>
<tr>
<td>CIEMAT/ES</td>
<td>LINCE</td>
<td>Loop</td>
<td>Long-term corrosion experiments and oxygen control system analysis</td>
<td>Yes</td>
<td>500°C</td>
<td>18 l/min</td>
<td>Two test sections</td>
<td>14</td>
</tr>
<tr>
<td>JAERI/JP</td>
<td>JLS</td>
<td>Static</td>
<td>Compatibility of materials</td>
<td>OCS partially</td>
<td>600°C</td>
<td>–</td>
<td>LBE inventory 170 l, electrical power 80 kW</td>
<td>13</td>
</tr>
<tr>
<td>JAERI/JP</td>
<td>JLBL-1</td>
<td>Loop</td>
<td>Corrosion studies and development of flow measurement techniques</td>
<td>H₂/H₂O</td>
<td>450°C</td>
<td>15 l/min</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>CRIEPI/JP</td>
<td>PbBi static corrosion</td>
<td>Static</td>
<td>Behaviour of static corrosion in Pb-Bi</td>
<td></td>
<td>700°C</td>
<td>–</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>MES/JP</td>
<td>MES-LOOP2001</td>
<td>Loop</td>
<td>Coolant purification, thermal-hydraulic and corrosion tests</td>
<td>H₂/H₂O – yes sensor</td>
<td>550°C</td>
<td>15 l/min</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>KAERI/KR</td>
<td>Not named</td>
<td>Loop</td>
<td>OCS, corrosion, thermal-hydraulics</td>
<td>Yes OCS yes sensor</td>
<td>550°C</td>
<td>3.6 m³/h</td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>SNU/KR</td>
<td>HELIOS</td>
<td>Loop</td>
<td>OCS, materials and thermal-hydraulics (natural circulation capabilities in PEACER-300)</td>
<td>Yes OCS</td>
<td>450°C</td>
<td>200 cm/s</td>
<td>HELIOS has been designed by thermo-hydraulics scaling of PEACER-300</td>
<td>23</td>
</tr>
<tr>
<td>ŘEZ/CZ</td>
<td>COLONRI I</td>
<td>Loop</td>
<td>Corrosion in different conditions</td>
<td>OCS indirectly</td>
<td>700°C</td>
<td>1-2 cm/s</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>ANL/USA</td>
<td>Natural convection quartz harp</td>
<td>Loop</td>
<td>Long-term corrosion in Pb/LBE; thermo-mechanical behaviour between materials and Pb/LBE</td>
<td>H₂/H₂O</td>
<td>800°C</td>
<td>0.01 m/s</td>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>

* CP = contact persons for the facilities. CP are listed at the end of the chapter.
Table 12.1. Summary of the international heavy liquid metal test facilities (cont.)

<table>
<thead>
<tr>
<th>Association/country</th>
<th>Name of the facility</th>
<th>Type of facility</th>
<th>Objectives</th>
<th>OCS – (\text{O}_2) probe</th>
<th>Tmax</th>
<th>Flow rate</th>
<th>Other information</th>
<th>CP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIT/US</td>
<td>H.H. Uhlig Corrosion Lab</td>
<td>Static/rotating disc</td>
<td>Corrosion mechanism, benchmarking corrosion/precipitation; oxygen sensors</td>
<td>O/He; H/He; H/(\text{H}_2)O</td>
<td>800°C</td>
<td>0-3 m/s</td>
<td>The liquid metal is contained in a ZrO(_2) crucible, capability of the crucible is 4 L</td>
<td>21</td>
</tr>
<tr>
<td>UnivLILLE/F</td>
<td>Mechanical Properties in Liquid Metals</td>
<td>Static</td>
<td>Monotonic and cyclic properties of structural alloys in liquid metals</td>
<td>No</td>
<td>600°C</td>
<td>Static</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>TIT/JP</td>
<td>LBE Corrosion</td>
<td>Loop</td>
<td>Material corrosion in flowing Pb-Bi, oxygen control technique, oxygen sensor, electromagnetic flow meter, ultrasonic flow meter</td>
<td>PbO</td>
<td>550°C</td>
<td>0.36 m(^3)/h</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>SCK(\text{\textbullet})CEN/B</td>
<td>LIMEST 1</td>
<td>Static</td>
<td>Mechanical testing of materials and oxide layers in LBE</td>
<td>Ar/H(_2)</td>
<td>500°C</td>
<td>Static</td>
<td>Calibration of oxygen sensors also foreseen</td>
<td>26</td>
</tr>
<tr>
<td>SCK(\text{\textbullet})CEN/B</td>
<td>LIMEST 2</td>
<td>Static</td>
<td>Mechanical testing of irradiated materials in LBE</td>
<td>Ar/H(_2)</td>
<td>500°C</td>
<td>Static</td>
<td>SSRT, constant and raising load, CGR</td>
<td>27</td>
</tr>
</tbody>
</table>

**Thermal-hydraulics facilities**

<table>
<thead>
<tr>
<th>Association/country</th>
<th>Name of the facility</th>
<th>Type of facility</th>
<th>Objectives</th>
<th>OCS – (\text{O}_2) probe</th>
<th>Tmax</th>
<th>Flow rate</th>
<th>Other information</th>
<th>CP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>FZK/D</td>
<td>THEADES</td>
<td>Loop</td>
<td>Single effects, beam window, window less, fuel elements, heat transfer</td>
<td>H(_2)/H(_2)O – yes</td>
<td>450°C</td>
<td>100 m(^3)/h</td>
<td>Height of the test sections 3.4 m</td>
<td>1</td>
</tr>
<tr>
<td>ENEA/I</td>
<td>CIRCE</td>
<td>Pool</td>
<td>Thermal-hydraulics, component development, large-scale exp. and liquid metal chemistry in pool config.</td>
<td>OCS yes – no (\text{O}_2) probe</td>
<td>450°C</td>
<td></td>
<td>8540 l of LBE</td>
<td>4</td>
</tr>
<tr>
<td>ENEA/I</td>
<td>CHEOPE 1</td>
<td>Loop</td>
<td>Thermal-hydraulics, cooling pin</td>
<td></td>
<td>500°C</td>
<td></td>
<td>900 l of LBE</td>
<td>4</td>
</tr>
<tr>
<td>RIT/SE</td>
<td>TALL</td>
<td>Loop</td>
<td>Thermal-hydraulics and heat transfer measurements</td>
<td>No OCS – yes sensor</td>
<td>550°C</td>
<td>2.5 m(^3)/h</td>
<td>Height of the test section: 6.8 m</td>
<td>11</td>
</tr>
<tr>
<td>JAERI/JP</td>
<td>JLBL-2</td>
<td>Loop</td>
<td>Flow studies in horizontal LBE target</td>
<td>No</td>
<td>&lt;450°C</td>
<td>50 l/min</td>
<td>Proof test of target – I</td>
<td>14</td>
</tr>
<tr>
<td>JAERI/JP</td>
<td>JLBL-3</td>
<td>Loop</td>
<td>Thermal-fluid test loop</td>
<td>Yes</td>
<td>450°C</td>
<td>500 l/min</td>
<td>Collaboration with MES</td>
<td>28</td>
</tr>
<tr>
<td>CRIEPI/JP</td>
<td>Pb-Bi Thermal-hydraulics</td>
<td>Loop</td>
<td>Heat transfer characteristics of Pb-Bi, gas lift pump performance in Pb-Bi flow characteristics of Pb-Bi/gas two-phase flow</td>
<td>No</td>
<td>300°C</td>
<td>6 m(^3)/h</td>
<td></td>
<td>15</td>
</tr>
</tbody>
</table>

* CP = contact persons for the facilities. CP are listed at the end of the chapter.
Table 12.1. Summary of the international heavy liquid metal test facilities (cont.)

<table>
<thead>
<tr>
<th>Association/country</th>
<th>Name of the facility</th>
<th>Type of facility</th>
<th>Objectives</th>
<th>OCS – O$_2$ probe</th>
<th>Tmax</th>
<th>Flow rate</th>
<th>Other information</th>
<th>CP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>LANL/US</td>
<td>DELTA</td>
<td>Loop</td>
<td>Corrosion tests in flowing LBE, corrosion/precipitation and system kinetics models, oxygen sensors and control systems, thermal-hydraulics experiments, components testing, data acquisition and control systems</td>
<td>Yes</td>
<td>550°C</td>
<td>2-5 m/s</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>UW/US</td>
<td>Wisconsin Tantalus facility</td>
<td>Loop</td>
<td>Multi-phase flow, heat transfer and flow stability/oscillations of steam/water injection into Pb/LBE</td>
<td>–</td>
<td>550°C</td>
<td>1-10 g/sec</td>
<td></td>
<td>22</td>
</tr>
<tr>
<td>KAERI/KR</td>
<td>Not named</td>
<td>Loop</td>
<td>OCS, corrosion, thermal-hydraulics</td>
<td>Yes OCS – yes sensor</td>
<td>550°C</td>
<td>3.6 m³/h</td>
<td>HELIOS was designed by thermo-hydraulics scaling of PEACER - 300</td>
<td>17</td>
</tr>
<tr>
<td>SNU/KR</td>
<td>HELIOS</td>
<td>Loop</td>
<td>OCS, materials and thermal-hydraulics (natural circulation capabilities in PEACER-300)</td>
<td>Yes OCS</td>
<td>450°C</td>
<td>200 cm/s</td>
<td>HELIOS was designed by thermo-hydraulics scaling of PEACER - 300</td>
<td>23</td>
</tr>
<tr>
<td>TIT/JP</td>
<td>LBE-H$_2$O Direct Contact</td>
<td>Appar.</td>
<td>Operation technique of steam gas lift pump type Pb-Bi-cooled fast reactor, thermal-hydraulics of Pb-Bi-water direct contact boiling flow</td>
<td></td>
<td>460°C</td>
<td>33.8 kg/h</td>
<td></td>
<td>25</td>
</tr>
</tbody>
</table>

* CP = contact persons for the facilities. CP are listed at the end of the chapter.
Contact persons

[1] Dr. Robert Stieglitz  
Institute for Nuclear and Energy Technologies (IKET)  
FZK  
Tel: +49 (0) 7247 / 82 3462  
Fax: +49 (0) 7247 / 82 4837  
Eml: robert.stieglitz@iket.fzk.de

[2] Dr. Juergen Konys  
Institute for Materials Research III (IMF III)  
FZK  
Tel: +49 (0) 7247 / 82 3720  
Fax: +49 (0) 7247 / 82 3956  
Eml: juergen.konys@imf.fzk.de

[3] Dr. Georg Mueller  
Institut für Hochleistungsimpuls und Mikrowellentechnik (IHM)  
FZK  
Tel: +49 (0) 7247 / 82 4669  
Fax: +49 (0) 7247 / 82 2256  
Eml: georg.Mueller@ihm.fzk.de

Cc to:  
Dr. Joachim U. Knebel  
Head, Programme Nuclear Safety Research (NUKLEAR)  
Tel: +49 (0) 7247 / 82 5510  
Fax: +49 (0) 7247 / 82 5508  
Eml: joachim.knebel@psf.fzk.de

[4] Dr. Antonio Aiello  
UTS Tecnologie Fisiche Avanzate – Sezione di Ingegneria Sperimentale (FIS ING)  
ENEA  
Tel: +39 0534 / 801380  
Fax: +39 0534 / 801250  
Eml: antonio.aiello@brasimone.enea.it

Cc to:  
Dr. Gianluca Benamati  
Head, Experimental Engineering Section  
UTS Tecnologie Fisiche Avanzate – Sezione di Ingegneria Sperimentale (FIS ING)  
ENEA  
Tel: + 39 0534 / 801423  
Fax: + 39 0534 / 801250  
Eml: gianluca.benamati@brasimone.enea.it

[5] Dr. Fanny Balbaud  
DEN/DPC/SCCME/LECNA  
CEA  
Tel: +33 (0)1 69 08 16 51  
Fax: +33 (0)1 69 08 15 86  
Eml: fanny.balbaud@cea.fr

DEN/DER/STR/LCEP  
CEA  
Tel: +33 (0)4 42 25 32 66  
Fax: +33 (0)4 42 25 72 87  
Eml: jean-louis.courouau@cea.fr

Cc to:  
Dominique Warin  
Head, Programme Nuclear Waste Toxicity Reduction  
DEN/DDIN/FITRA  
CEA  
Tel: +49 (0) 7247 / 82 5510  
Fax: +49 (0) 7247 / 82 5508  
Eml: Dominique.warin@cea.fr
[7] Dr. Heike Glasbrenner
Spallation Neutron Source Division (ASQ)
PSI
Tel: +41 (0) 56 310 4712
Fax: +41 (0) 56 310 3131
Eml: heike.glasbrenner@psi.ch

Cc to:
Dr. Friedrich Gröschel
Head
MEGAPIE Project
PSI
Tel: +41 (0) 56 310 2196
Fax: +41 (0) 56 310 3131
Eml: friedrich.groeschel@psi.ch

[8] Dr. Paul Schuurmans
Reactor Physics and MYRRHA Department
SCK•CEN
Tel: +32 (0) 14 / 33 22 93
Fax: +32 (0) 14 / 32 15 29
Eml: Paul.Schuurmans@sckcen.be

Cc to:
Dr. Hamid Aït Abderrahim
Head
Reactor Physics and MYRRHA Department
SCK•CEN
Tel: +32 (0) 14 / 33 22 77
Fax: +32 (0) 14 / 32 15 29
Eml: Haitabde@sckcen.be

[9] Danislav Sapundjiev
Reactor Materials Research Department
SCK•CEN
Tel: (+32) 14 33 34 15
Fax: (+32) 14 32 13 36
Eml: dsapundj@sckcen.be

[10] Dr. Dolores Gomez-Briceno
Materials Project Head
CIEMAT
Tel: +34 91 3466605
Fax: +34 91 346661
Eml: lola.gomezbriceno@ciemat.es

[11] Dr. Weimin Ma, Dr. Aram Karbojian
Division of Nuclear Power Safety
KTH
Tel: +46-8-790 92 54
Fax: +49-8-790 91 97
Eml: ma@egi.kth.se, aram@egi.kth.se

Cc to:
Prof. Bal Raj Sehgal
Head
Nuclear Power Safety Division
KTH
Tel: +49-8-790 9252
Fax: +49-8-790 9197
Eml: sehgal@egi.kth.se

[12] Dr. Ning Li
Lead-alloys Technology Development
AFCI/Gen IV
Tel: +1 505 665 6677
Fax: +1 505 667 7443
Eml: ningli@lanl.gov

Cc to:
Mr. Michael W. Cappiello
Program Manager
AFCI-LANL
Tel: +1 505 665 6408
Fax: +1 505 667 7443
Eml: mcappiello@lanl.gov

[13] Dr. Yuji Kurata
Center for Proton Accelerator Facilities
JAERI
Tel: +81 (0) 29 / 282 5059
Fax: +81 (0) 29 / 282 6487
Eml: ykurata@popsvr.tokai.jaeri.go.jp
[14] Dr. K Kikuchi
Center for Proton Accelerator Facilities
JAERI
Tel: +81 (0) 29 / 282 5058
Fax: +81 (0) 29 / 282 6489
Eml: kikuchi@popsvr.tokai.jaeri.go.jp

[15] Dr. Yoshihisa Nishi
Central Research Institute of Electric Power Industry (CRIEPI)
Komae Research Laboratory
Nuclear Energy Systems Department
Tel: +81 3 3480-2111
Fax: +81 3 3480 2493
Eml: y-nishi@criepi.denken.or.jp

Cc to:
Dr. Izumi Kinoshita
Central Research Institute of Electric Power Industry (CRIEPI)
Komae Research Laboratory
Nuclear Energy Systems Department
Tel: +81 3 3480-2111
Fax: +81 3 3480 2493
Eml: kinosita@criepi.denken.or.jp

[16] Mr. Teruaki Kitano
Engineering Department
Nuclear Energy Systems Division
Mitsui Engineering and Shipbuilding Co., Ltd.
Tel: 03-3675-7286
Fax: 03-3675-7129
Eml: kitano@mes.co.jp

Cc to:
Mr. Kin-ya Kamata
Tamano Technology Center
Technical Research & Development HQ
Mitsui Engineering and Shipbuilding Co., Ltd.
Tel: +81-863-31-9613
Fax: +81-863-31-4819
Eml: kama@mj.mes.co.jp

[17] Dr. C.H. Cho
HYPER Team
KAERI
Tel: +82 - 42-868-2914
Fax: +82 - 42-868-2080
Eml: chcho@kaeri.re.kr

Cc to:
Dr. T.Y. Song
HYPER Team
KAERI
Tel: +82 - 42-868-8924
Fax: +82 - 42-868-2080
Eml: tysong@kaeri.re.kr

[18] Dr. Anna Brožová
Div. of Integrity and Technical Engineering
Dept. of Structural Properties and Corrosion
Řež
Tel: (+420-2) 6617 3432
Fax: (+420-2) 2094 0519
Eml: bro@ujv.cz

Cc to:
Dr. Dalibor Kárník
Div. of Integrity and Technical Engineering
Dept. of Structural Properties and Corrosion
Řež
Tel: (+420-2) 6617 2617
Fax: (+420-2) 2094 0519
Eml: kar@ujv.cz
[19] Dr. Anthony Hechanova
Harry Reid Center for Environmental Studies
University of Nevada, Las Vegas
Tel: +1 702-895-1457
Fax: +1 702-895-3094
Eml: Hechanova@unlv.nevada.edu

[20] Dr. Jude Mary Runge
Chemical Engineering Division
Argonne National Laboratory
Tel: +001 630-252-3430
Fax: +001 630-252-9917
Eml: runge@cmt.anl.gov

Cc to:
Dr. Douglas Crawford
Argonne National Laboratory
Tel: +001 208-533-7456
Fax:
Eml: douglas.crawford@anl.gov

[21] Professor Ronald G. Ballinger
Dept. of Nuclear Engineering
Dept. of Materials Science and Engineering
H.H. Uhlig Corrosion Laboratory
Massachusetts Institute of Technology
Tel: +1 617-253-5118
Fax: +1 617 253 0807
Eml: hvymet@mit.edu

[22] Dr. Michael Corradini
Engineering Physics
University of Wisconsin
Tel: 608-263-1648
Fax: 608-263-7451
Eml: Corradini@engr.wisc.edu

[23] Prof. Il Soon Hwang
Nuclear Materials Laboratory
Nuclear Engineering Department
Associate Director
Nuclear Transmutation Energy Research Center of Korea (NUTRECK)
Tel: +82-2-880-7215
Fax: +82-2-889-2688
Eml: hisline@snu.ac.kr

[24] Prof. Jean-Bernard Vogt
Laboratoire de Métallurgie Physique et Génie des Matériaux (LMPGM)
Université des Sciences et Technologies de Lille (USTL) UMR CNRS 8517
Tel: +33 (0)3 20 43 40 35
Fax: +33 (0)3 20 43 40 35
Eml: jean-bernard.vogt@univ-lille1.fr

Cc to:
Dr. Ingrid Serre
Laboratoire de Métallurgie Physique et Génie des Matériaux (LMPGM)
Université des Sciences et Technologies de Lille (USTL) UMR CNRS 8517
Tel: +33 (0)3 20 43 66 06
Fax: +33 (0)3 20 33 61 48
Eml: ingrid.serre@univ-lille1.fr

[25] Professor Minoru Takahashi
Research Laboratory for Nuclear Reactors
Tokyo Institute of Technology
Tel:
Fax:
Eml: mtakahas@nr.titech.ac.jp
[26] Danislav Sapundiev  
Reactor Materials Research Department  
SCK•CEN  
Tel: (+32) 14 33 34 15  
Fax: (+32) 14 32 13 36  
Eml: dsapundj@sckcen.be

Cc to:  
Abdou Al Mazouzi  
Reactor Materials Research Department  
SCK•CEN  
Tel: (+32) 14 33 30 96  
Fax: (+32) 14 32 12 16  
Eml: aalmazou@sckcen.be

[27] Rik Wouter Bosch  
Reactor Materials Research Department  
SCK•CEN  
Tel: (+32) 14 33 34 17  
Fax: (+32) 14 32 13 36  
Eml: rik-wouter.bosch@sckcen.be

Cc to:  
Abdou Al Mazouzi  
Reactor Materials Research Department  
SCK•CEN  
Tel: (+32) 14 33 30 96  
Fax: (+32) 14 32 12 16  
Eml: aalmazou@sckcen.be

[28] Dr. K. Kikuchi  
Japan Atomic Energy Agency (JAEA)  
Tel: +81 29 282 5058  
Fax: +81 29 282 6489  
Eml: kikuchi.kenji21@jaea.go.jp

Cc to:  
Dr. M. Ono  
Tel: +81 3 3675 7354  
Fax: +81 3 3675 7129  
Eml: ono@mes.co.jp
Chapter 13
SAFETY GUIDELINES*

Lead is a highly toxic substance [EPA] [CIS-ILO]. Exposure to lead can cause irreversible health effects before signs and symptoms are seen or felt [Lewis, 1985]. Rules and regulations, safety controls and practices have been developed to mitigate the lead hazards over the years. Consequently, many occupational uses of lead now pose little risk of exposure if one takes precautions and follows procedures. However, when lead is used in a manner that is different from routine operations, the risk of exposure may be increased. For researchers developing lead-alloy technologies, it is imperative that safety principles are closely observed, proper protective measures taken and formal procedures followed.

In the context of lead-alloy coolant technology, lead oxide hazards may exist as well. Lead oxide exists in one of the two forms: red to reddish-yellow tetragonal crystals stable at room temperature, and yellow orthorhombic crystals stable at above 489°C. Lead oxide presents severe health hazards, especially in the form of lead fumes or dusts, and should be treated with the same caution as with lead.

On the other hand, bismuth does not present severe hazards except under several special circumstances. For example, bismuth dust or powder can be flammable or even explosive at high concentrations and exposed to heat or flame. Generally bismuth may cause mild eye, skin and gastrointestinal irritation. Due to its low hazard ratings, the measures taken to mitigate lead hazards should be sufficient when bismuth is used together with lead. Hence bismuth hazards and controls will not be discussed here.

It is worth noting that the safety practices are tightly linked to good and meaningful outcomes of experiments and tests because they ensure proper control of the environment. Some practical implementation of the coolant technology, on the other hand, can produce unique hazards if not done correctly.

This chapter outlines the effects of lead on human health and environment, the general rules and regulations governing the safe use and disposal of lead in many OECD countries [OSHA], some common safety measures and procedures, and recommendations for routine R&D operations illustrated with several typical experiments. It should be used as a starting point to specific information available in the references. The scope is based on a balance between brevity (ease of use) and completeness (usefulness), and is much more extensive than that of the Materials Safety Date Sheets (MSDS). The main text is based on the training manual for lead awareness at the Los Alamos National Laboratory [Grogin, 2001], with references on country-specific rules and regulations recommended by the expert working group members. A very comprehensive discussion on air-borne lead hazards can also be found in a position paper by a Working Group on Lead, Commission of EU [CEC, 1997]. Many other reports have detailed information and analyses on different aspects of lead, waste and environment (e.g. [Holm, 2002], [WHO, 1989]).

* Chapter lead: Ning Li (LANL, USA).
It should be pointed out that under proton and neutron irradiation, lead and lead-alloys all present varied, sometimes severe, radioactive hazards. These hazards and the conditions leading to their occurrence are complex and often system or alloy specific, e.g. \(^{210}\)Po from irradiated bismuth [Cullen, 2003]. They are not covered in this chapter. However, this is an extremely important topic for lead-alloy nuclear coolant application and should warrant a separate and detailed review in the future.

13.1 Effects of lead on human health and environment

Lead can enter human body in three different ways: inhalation (breathing), ingestion (eating or drinking), or absorption (through skin).

**Figure 13.1.1. Absorption and storage of lead in human body [NSW]**

Inhalation of airborne lead is the most common means by which lead can enter human body in the workplace. Inhalation can occur when lead is scattered in the air as a dust, fume, or mist. Inhaling small particles of lead allows the material to travel into lungs, where it can be absorbed into the bloodstream.

The second most common way is by ingestion (swallowing). Ingestion of lead in the workplace is nearly always the result of poor hygiene practices. Lead can be ingested by handling food, using cigarettes or chewing tobacco, or applying cosmetics when hands are contaminated with lead.
Absorption of lead through the skin is rare, but it can occur if skin is exposed to certain organic forms of lead or if certain chemicals (such as dimethyl sulfoxide) capable of transporting heavy metals through the skin are present.

All of the lead that deposits in lungs and 10-15% of the lead ingested enters bloodstream. In pregnant women, the amount of lead absorbed into the bloodstream through ingestion can increase to 50%. Once in the bloodstream, lead circulates throughout the body and is excreted at a steady rate. As exposure to lead continues, the amount stored in the body will increase if absorption is more than excretion. Of the total amount of lead stored in the body, about 90% is found in the bones and teeth. If no further uptake occurs, accumulated lead is slowly released from the blood and soft tissues over a period of months, but is only released from the bones and teeth over a period of decades. If uptake continues, stored lead will eventually reach toxic levels, a condition known as lead intoxication. Accumulated lead can cause irreversible body damage before showing any signs or symptoms.

Exposure to lead through inhalation or ingestion can cause serious health effects in a variety of body systems. Such health effects may arise from acute (short-term) or chronic (long-term) exposures. The severity of an exposure depends upon the amount, or dose, of lead that enters human body. A short-term, high-dose lead exposure can cause kidney, nerve, and brain damage that may lead to seizures, coma, and death within a matter of days. Workplace exposures of this type are extremely rare but not impossible. Signs and symptoms of acute lead exposure are similar to many common ailments and, as a result, may not be immediately recognised. Signs and symptoms of acute lead exposure may include: blood in the urine or stool, paralysis, coughing, restlessness, digestive disorders, skin or eye irritation, disorientation, sleeplessness, drooling, sweating, fever and chills, thirst, frequent urination, tingling sensation, headache, vomiting, loss of memory, weakness, metallic taste, yellowing of the skin and eyes (jaundice), and muscle pain.

There is a condition specific to exposure to lead fumes called metal fume fever. It is an influenza-like illness caused by inhalation of freshly formed metal oxide particles with sizes below 1.5 microns, and usually between 0.02-0.05 microns. Symptoms may be delayed 4-12 hours and begin with a sudden onset of thirst, and a sweet, metallic or foul taste in the mouth. Other symptoms may include upper respiratory tract irritation accompanied by coughing and a dryness of the mucous membranes, lassitude and a generalised feeling of malaise. Fever, chills, muscular pain, mild to severe headache, nausea, occasional vomiting, exaggerated mental activity, profuse sweating, excessive urination, diarrhoea and prostration may also occur. Tolerance to fumes develops rapidly, but is quickly lost. All symptoms usually subside within 24-36 hours. Resistance to the condition develops after a few days of exposure, but is quickly lost in 1 or 2 days.

Long-term exposures to lead can damage the blood-forming system, impairing the replenishment of blood cells and the blood’s ability to carry oxygen; the central nervous system and the brain; the kidneys, to the extent that kidney dialysis may be needed; and reproductive systems in both men and women. Signs and symptoms of chronic lead exposure can include: anaemia, lack of co-ordination, blue-black lines on the gums, twitching, high blood pressure, visual disturbances, loss of appetite, and weight loss.

Chronic, high-dose exposures can impair the reproductive system of both men and women. Effects include decreased sex drive, impotence, and sterility in men and decreased fertility and abnormal menstrual cycles in women. There is an increased risk of miscarriage and stillborn children in women whose husbands were exposed to lead or who were exposed to lead themselves. There is also an increased risk of birth defects, mental retardation, behavioural disorders, or death during the first year in children born to such parents.
Lead may enter the environment during its usage and disposal [EPA]. The initial means of entry is via the atmosphere. Lead will be retained in the upper 2-5 cm of soil, especially soils with at least 5% organic matter or a pH 5 or above. It is expected to slowly undergo speciation to the more insoluble sulphate, sulphide, oxide, and phosphate salts.

Lead enters water from atmospheric fallout, runoff or wastewater. Metallic lead is attacked by pure water in the presence of oxygen, but if the water contains carbonates and silicates, protective films are formed preventing further attack. That which dissolves tends to form ligands. Lead is effectively removed from the water column to the sediment by adsorption to organic matter and clay minerals, precipitation as insoluble salt, and reaction with hydrous iron and manganese oxide. Under most circumstances, adsorption predominates.

Lake sediment micro-organisms are able to directly methylate certain inorganic lead compounds. Under appropriate conditions, dissolution due to anaerobic microbial action may be significant in subsurface environments. The mean percentage removal of lead during the activated sludge process was 82% and was almost entirely due to the removal of the insoluble fraction by adsorption onto the sludge and to a much lesser extent, precipitation.

The most stable form of lead in natural water is a function of the ions present, the pH, and the redox potential. In oxidising systems, the least soluble common forms are probably the carbonate, hydroxide, and hydroxycarbonate. In reduced systems where sulfur is present, PbS is the stable solid.
The solubility of Pb is 10 ppb above pH 8, while near pH 6.5 the solubility can approach or exceed 100 ppb. Pb(0) and Pb(+2) can be oxidatively methylated by naturally occurring compounds such as methyl iodide and glycine betaine. This can result in the dissolution of lead already bound to sediment or particulate matter.

Figure 13.1.3. Sources and pathways of lead in the environment [NSW]

Elevated levels of lead in the water can cause reproductive damage in some aquatic life and cause blood and neurological changes in fish and other animals that live there.

Lead does not appear to bioconcentrate significantly in fish but does in some shellfish such as mussels. Evidence suggests that lead uptake in fish is localised in the mucous on the epidermis, the dermis, and scales so that the availability in edible portions do not pose a human health danger.

Wild and domestic animals can ingest lead while grazing. They experience the same kind of effects as people who are exposed to lead. Low concentrations of lead can slow down vegetation growth near industrial facilities.

13.2 Rules and regulations

Lead is a technologically important metal throughout the history. It is widely used in many industries and applications. Because of this wide presence and its toxic nature, lead work is also one the most regulated fields of labour. There are many rules and regulations in all industrial countries governing the use of lead.

Since regulations are country-specific and compliance is strictly required, it is beyond the scope of this handbook to present a comprehensive review of this topic. A compilation of the most significant standards and requirements is presented in the following table. Researchers should consult safety authorities within own organisations/countries to determine specific requirements for compliance.
However, there are several common features worth highlighting. First, since inhalation of airborne lead is the most common pathway for lead to enter human bodies, all regulations place a maximal allowable concentration (for an 8 hour shift, it is variably termed PEL – permissible emission level, or MPC – maximum permissible concentration, or MAK-value – maximum allowable concentration in workstation at any time). PEL/MPC varies from 50-100 μg/m³, while MAK-value ranges from 100-150 μg/m³.

In practice, if we use the lead and LBE vapour pressures from the literature [Lyon, 1952][Morita, 2004], the 50-100 μg/m³ PEL corresponds to 530-550°C for LBE and 500-520°C for Pb. Special care and controls must be taken to conduct experiments with exposed LBE and Pb above these temperatures. For airborne lead levels below PEL, the allowable work duration is lengthened proportionally so the total exposure equals to 8 hr times PEL.

Second, due to enhanced health threat (impairment of reproductive system and damages to children), the standards for young persons and pregnant women are more stringent. The Pb in blood (PbB) levels that require continued monitoring and work stoppage are lower for workers with heightened risks.

The monitoring frequency for airborne lead and PbB varies depending on severity from pervious measurement or whether changes in procedures and controls take place. It varies from 3 to 12 months, or longer when no changes occur. There are generally requirements on how long the monitoring and medical records should be kept for the workers.

There are rules and regulations governing the limit value and monitoring of lead in ambient air and in wastes.

National Ambient Air Quality Standard (NAAQS) is set by US EPA for pollutants that are considered to be harmful to public health and the environment; the NAAQS for lead is 1.5 μg/m³, maximum arithmetic mean averaged over a calendar quarter [EPA].

Commission of EU established a limit value for Pb in ambient air of 2 μg Pb/m³ [EU]. Some countries have reduced the limit to 0.5 μg/m³. The sampling method is to collect atmospheric particles on a filter for subsequent determination of lead content. The reference method of analysis is atomic absorption spectrometry.

US EPA regulation sets the limit of Pb in solid waste to be 5 mg/L beyond which the waste is considered hazardous (EPA HW No. D008; CAS No. 2: 7439-92-1) [CFR]. This puts most of the lead contaminated materials in coolant R&D in the category of hazardous wastes, including residues from polishing corrosion test specimens with small amount of Pb adhered. EU has been moving toward lead-free solder so the requirements might become even more stringent. The concentration limit in consideration is 0.1 wt.% for EU and Japan [SolderTec, 2003].

For surface contamination, the following wipe sample clearance guidelines are recommended by US HUD [LLNL, 2005]:

- <100 μg/ft² (0.108 μg/cm²) on uncarpeted floors;
- <500 μg/ft² (0.538 μg/cm²) on interior window sills (stools);
- <800 μg/ft² (0.861 μg/cm²) on window troughs (where the sash sits when closed);
- <800 μg/ft² (0.861 μg/cm²) on exterior concrete.
These clearance guidelines are based on hazards to children, and are extremely low. So in R&D work, higher limits may be acceptable at the discretion of responsible industrial hygienist. Although in common laboratory settings, Pb vapour presence is minimal, long-term exposure without proper periodic clean-up could lead to high levels of Pb surface contamination.

Irradiated Pb and LBE may be considered low-level radioactive wastes. The disposal of such wastes is more difficult and their disposition sites very limited and country dependent. It is beyond the scope of this chapter and should be treated in the future in the context of decommissioning and decontamination (D&D).

13.3 Common safety controls and practices

General controls can be used to reduce the potential for occupational exposure to lead. They can be categorised as engineering controls and administrative controls. Additionally there may be specific controls unique to the job. Industrial hygienists or other relevant safety specialists should be consulted about these controls, and approvals sought for operations involving lead.

Engineering controls are mechanical or structural systems used to minimise hazards. They include ventilation systems (e.g. fume hoods), isolation systems (e.g. glove boxes), adhesive mats at doorways, hygiene facilities (e.g. hand-washing basins), etc.

Administrative controls are used to direct, restrict, or modify behaviour to prevent or minimise exposure to hazards. Specific requirements vary, but they generally include plans, procedures and permits, safe work practices, housekeeping, postings, access controls, and training.

Plans, procedures and permits define the operating conditions that one may encounter and special precautionary measures to minimise workplace exposure to lead. When there is a potential for lead to become airborne in a manner that potentially increases risk of exposure, the activity hazard analysis or hazard control plan should identify the hazard and specify controls.

There are several general safe work practices and housekeeping rules to minimise or prevent exposure to lead, including:

- Wash hands and face before eating, drinking, or applying cosmetics.
- Use only high-efficiency particulate air (HEPA) filter vacuums.
- Remove work clothes before entering eating areas, or use HEPA vacuums to clean dust off the clothes.
- Maintain all surfaces as free as practicable of accumulation of lead dust;
- Do not dry-sweep areas where lead may be present.
- Do not wear work clothes beyond the work area to prevent contamination.

For controls such as washing facilities, clean changing areas, separate clothes lockers, and showers to remain effective, workers must use them routinely and correctly.

Postings and access controls must be used in each work area where the permissible level is exceeded or as a precautionary measure where lead is present. Some areas may need access control to prevent unqualified personnel from entering.
**Table 13.2.1. Regulations governing the safe use of lead in selected countries**

**PEL – Permissible Exposure Level, AL – Action Level**

<table>
<thead>
<tr>
<th>Country/region</th>
<th>Regulations</th>
<th>In air, max permissible Exposure level for 8-hr shift (PEL, microgram/m³)</th>
<th>In air, action level (AL, microgram/m³)</th>
<th>Monitoring frequency (month)</th>
<th>Max Pb in blood (PbB, microgram/dl)</th>
<th>Record keeping (yr)</th>
<th>Regular worker</th>
<th>Worker planning &amp; children</th>
</tr>
</thead>
<tbody>
<tr>
<td>US</td>
<td>OSHA standards (<a href="http://www.osha.gov">www.osha.gov</a>), 29 CFR, 1910.1025 – all occupational exposure to lead, and 1926.62 – all construction work, where an employee may be occupationally exposed to lead</td>
<td>60 (100 MAK-value)</td>
<td>80</td>
<td>3</td>
<td>6</td>
<td>Only when new risks are introduced through change of work, control</td>
<td>The longer of 40 or duration of employment+20 (30 for construction worker)</td>
<td>40</td>
</tr>
<tr>
<td>Switzerland</td>
<td>Safety at Work is regulated by Federal Law (<a href="http://www.sapo.admin.ch/">http://www.sapo.admin.ch/</a>); Classification of products is in the competence of the Federal Government (<a href="http://www.bag.admin.ch/">http://www.bag.admin.ch/</a>); Surveillance that regulations are applied is in the competence of SUVA (<a href="http://www.suva.ch">http://www.suva.ch</a>)</td>
<td>100 (workers &lt; 18 years of age, pregnant women, atomic persons excluded from working in areas &gt; PEL)</td>
<td>50</td>
<td>2.6 depending on severity of exposure to be agreed upon with surveillance body</td>
<td>12</td>
<td>12</td>
<td>70 (male, female &gt; 45 years of age)</td>
<td>40 (female &lt; 45 years of age)</td>
</tr>
<tr>
<td>EU</td>
<td>EU Directives (<a href="http://europa.eu.int/legislation/index_en.htm">http://europa.eu.int/legislation/index_en.htm</a>)</td>
<td>150</td>
<td>75</td>
<td>3</td>
<td>3</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>France</td>
<td>EU Directives (<a href="http://europa.eu.int/legislation/index_en.htm">http://europa.eu.int/legislation/index_en.htm</a>)</td>
<td>150</td>
<td>75</td>
<td>3</td>
<td>3</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Germany</td>
<td>EU Directives (<a href="http://europa.eu.int/legislation/index_en.htm">http://europa.eu.int/legislation/index_en.htm</a>)</td>
<td>150</td>
<td>75</td>
<td>3</td>
<td>3</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sweden</td>
<td>Swedish Standards for Lead, APS 1982:17, Swedish Standards for Air Control, APS 1988:3, APS 2000:3 (<a href="http://www.av.se">www.av.se</a>)</td>
<td>50 (100 MAK-value)</td>
<td>100</td>
<td>1st 6 month, inspection required; afterwards, if Pb in air &lt; 0.5 PEL, no more inspection is needed; if 0.5 PEL &lt; Pb in air &lt; 1/5 PEL, the authority decides the monitoring frequency; if 1/5 PEL &lt; Pb in air &lt; 1/2 PEL, inspection is required every one year</td>
<td>3 months if exposure from lead alkyls, or previous measurement &gt; 100 microgram/m³</td>
<td>12</td>
<td>12</td>
<td>40 (young), 60 (others) (action levels: 40/50)</td>
</tr>
<tr>
<td>UK</td>
<td>The Control of Lead at Work Regulations 2002 (<a href="http://www.hmso.gov.uk/si/si2002/20022676.htm">http://www.hmso.gov.uk/si/si2002/20022676.htm</a>)</td>
<td>150 (100 lead alkyls)</td>
<td>100</td>
<td>3 months if exposure from lead alkyls, or previous measurement &gt; 100 microgram/m³</td>
<td>5 from date made</td>
<td>3 months</td>
<td>40 (young), 60 (others) (action levels: 40/50)</td>
<td>30 (action level 25)</td>
</tr>
<tr>
<td>Japan</td>
<td>Safety at work is regulated by Japanese law and ordinance (<a href="http://www.chemlaw.co.jp/">http://www.chemlaw.co.jp/</a>), English version (<a href="http://www.chemlaw.com/Pub/LawLink/humare_1.html">http://www.chemlaw.com/Pub/LawLink/humare_1.html</a>)</td>
<td>100</td>
<td>12</td>
<td>5</td>
<td>5</td>
<td>40</td>
<td>70</td>
<td>40</td>
</tr>
<tr>
<td>S. Korea</td>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Russian</td>
<td></td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Belgium</td>
<td>Exposure limits (<a href="http://meta.fgov.be/pdf/3pdenl/kflg03.pdf">http://meta.fgov.be/pdf/3pdenl/kflg03.pdf</a>)</td>
<td>150</td>
<td></td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>40</td>
<td>70</td>
</tr>
</tbody>
</table>
Training is required for all personnel subject to lead exposure. Typically it consists of two components: a general lead awareness training covering the topics outlined here, and a facility or task specific training provided by supervisors or facilities.

Personal protective equipment (PPE) is secondary protection that is used when other control measures are not feasible or not sufficiently effective at reducing exposures to lead. PPE can include coveralls, gloves, a face shield or vented goggles, booties, and respirators. In case respiratory protection is needed, proper training will be necessary.

When working with molten lead and lead-bismuth, toxic lead fumes are usually present, and the appropriate respirator should be selected if the concentration of fumes is above the permissible limit (PEL). Table 13.3.1 is based on US OSHA standards and represents the minimal respiratory protection at each action level [OSHA].

<table>
<thead>
<tr>
<th>Airborne concentration of lead or condition of use</th>
<th>Required respirator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not in excess of 0.5 mg/m³ (10X PEL).</td>
<td>Half-mask, air-purifying respirator equipped with high efficiency filters.²³</td>
</tr>
<tr>
<td>Not in excess of 2.5 mg/m³ (50X PEL).</td>
<td>Full face-piece, air-purifying respirator with high efficiency filters.³</td>
</tr>
<tr>
<td>Not in excess of 50 mg/m³ (1000X PEL).</td>
<td>(1) Any powered, air-purifying respirator with high efficiency filters³; or (2) Half-mask supplied-air respirator operated in positive-pressure mode.²</td>
</tr>
<tr>
<td>Not in excess of 100 mg/m³ (2000X PEL).</td>
<td>Supplied-air respirators with full face-piece, hood, helmet, or suit, operated in positive pressure mode.</td>
</tr>
<tr>
<td>Greater than 100 mg/m³, unknown concentration or fire fighting.</td>
<td>Full face-piece, self-contained breathing apparatus operated in positive-pressure mode.</td>
</tr>
</tbody>
</table>

¹ Respirators specified for high concentrations can be used at lower concentrations of lead.
² Full face-piece is required if the lead aerosols cause eye or skin irritation at the use concentrations.
³ A high efficiency particulate filter means 99.97% efficient against 0.3 micron size particles.

13.4 Safe operations in HLM R&D

Using lead in heavy liquid metal coolant technology R&D has many aspects of operations that can be hazardous if proper controls are absent and procedures are not followed. The hazards are multiplied many times in radiation environment, when alpha-emitting polonium-210, radioactive mercury isotopes and others are produced (see Chapter 8). Establishing the safety envelop and operating procedures, and getting approvals from safety authorities can be very labour intensive and time consuming, as the MEGAPIE project has demonstrated. This section, however, will not cover that but instead use several typical experimental operations with no irradiation to illustrate some safety practices in the more routine use of lead and LBE for HLM R&D. These are from observations and practices of many experiments and test facility operations around the world.
Many laboratories use small containers of LBE or lead to conduct experiments in the study of corrosion, wetting, embrittlement, oxygen control, etc. The generic operation steps may include setting up apparatus, preparation, melting, filling, insertion, sealing, heating, gas injection, cooling, opening, extraction, cleaning, and freezing. Transferring, draining, circulating, etc. are typically used in larger test loops and facilities, so covered separately later.

Setting up apparatus: The first consideration should be the location of the experiment and its environment. It should be in a dedicated laboratory or area separate from offices and eating areas with good ventilation and nearby washing facilities. The area should have non-porous, clean and uncluttered surfaces and walls to facilitate cleanup. Since leakage and spillage can occur, it is advisable to have metal drain pans underneath the apparatus and handling operations. If hoods or other active ventilation systems are used, HEPA filters should be installed.

The access should be controlled with proper warnings and contact information posted at prominent locations, including entrances, exits and next to the experiments. If large quantities of HLM are used, sticky mats on the floor at the exits may be used to limit contamination.

Periodic cleaning should be performed to eliminate deposited lead or its oxides. Use wet wipes for surfaces, and HEPA-filtered vacuum for floors. If a laboratory has been used for long time without frequent cleaning, surface sampling should be conducted to determine levels of contamination before cleaning is commenced.

Preparation: Solid LBE or lead ingots are typically used. Small amount of surface oxides can usually be dissolved into the melt (sometimes desirable if higher oxygen concentrations are needed), or cleaned up with mechanical means from the melt (e.g. picked up by a wire mesh scoop). If there is too much oxide, e.g. from long-term exposure to the environment, they should be discarded. Cleaning oxides in solid form may produce dangerous air-borne lead dust, and should be avoided.

Melting: Melting ingots into a crucible or a vessel is straightforward. However, melting solidified LBE or lead in a container requires some caution and well-planned procedures. There can be significant differential volume expansion during heat-up of HLM and container, leading to stresses that in some situations cause crack or rupture. HLM should be melted from free surfaces into more confined volumes. For large containers, separate heating zones with correct heating sequences should be used. Some design features, e.g. a few degrees of slant in a melting tank wall (expanding toward the top), are better suited than the others (e.g. a straight cylindrical tank is not as accommodating). A horizontal cylindrical melting tank more than half filled is not a good configuration. Due to such considerations, HLM is usually drained from test apparatus with complex internal structured for freezing and melting.

Filling: If a large amount of LBE or lead is used for the first time, a pre-melting and transfer device, draining from the bottom into the experimental apparatus, is recommended. Many suspended impurities, including sludge of oxides, can be removed from the free surface by mechanical means. Such operations should be carried out at temperatures as low as possible, i.e. just high enough to prevent accidental freezing and plugging. The specific temperatures depend on the setup, e.g. heating of the transfer line and the receiving vessel, but usually should be 150-180°C or slightly higher for LBE, and 380-400°C for lead. Such tasks can be carried out in open vessels, but the operators should wear respirators if more than a few kg of HLM is involved, and should in principle have air sampling done as well. While the vapour pressures at these temperatures are below permissible emission levels (PEL), the handling may create high levels of dusts, including lead oxides. Cleaning the surrounding afterwards is necessary to prevent the spread of contaminations. Vacuuming with a HEPA-filtered vacuum cleaner for loose dusts and wet wiping of exposed surfaces are recommended.
The vessels and pipes to be filled should be properly pre-heated to temperatures not too different from the melt. Difference of a few tens of degrees is acceptable, but 50°C or more may produce thermal shocks that could damage the apparatus or sensors. There can be mitigation measures (e.g. use of bellows for joints) and procedural control (e.g. slow fill when accidental freezing can be excluded) deployed to reduce such effects. If there are areas not very accessible to pre-heating (e.g. pipes inside a vessel), caution must be taken to prevent accidental freezing (e.g. use a higher melt temperature for filling).

**Insertion:** Sensors, test samples and gas lines are often inserted after the filling. This should be performed at the low temperatures. Since HLM is heavier than most materials, there will be some buoyancy so the fixtures should be sturdy and can prevent upward turning. Hanging is not an option here. At this stage, the free surfaces of HLM should have been cleaned up already so the insertion does not contaminate the undersides with oxides and other floating impurities.

For all the above operations involving open vessels, temperature should be kept low both for safety reasons, and for avoiding excessive oxidation. While using an inert heavy cover gas (e.g. Ar) to reduce oxidation may be desirable, it is not necessary.

**Sealing:** Due to the needs for safety and good coolant chemistry control, tight seals are essential for experiments and operations. External rotating seals should be avoided. Flanges with gaskets in contact with high temperature HLM should be avoided as well, although some have worked reasonably well (graphite or spiral wound steel gaskets). Since even small ingress of air will contaminate the HLM, a slightly positive cover gas pressure should be maintained during normal operations.

Due to relaxation of bolts from thermal cycles, flanges will loosen over time. There should be a periodic retightening scheduled and performed. If leakage does occur, the experiment should be stopped, HLM drained into a melt tank, and apparatus cooled down before repair and cleanup is performed. Liquid metal leakage detection can be based on simple conductivity probes in areas surrounding flanges or joints or likely collection basins, or inferred from loss of volume through level sensors, and loss of pressure.

**Heating:** Heating up the HLM in the molten state is quite simple but may have consequences beyond the obvious. Very rapid heat-up may be detrimental to some components, especially ceramic parts (such as oxygen sensors). There is no definitive rules reported, but a less than 50°C/hr heating rate is recommended for some Russian-made oxygen sensors. We have used much more rapid heating rates in small experiments with simple configurations. For large facilities, this should be determined carefully with analyses, simulations and testing.

Due to rapidly increasing solubility of elements in HLM with temperature, surface slags, especially lead oxides, will decrease and disappear. Oxidation of materials will also consume oxygen and clean up HLM surfaces. If no deliberate oxygen addition or air ingress takes place, the HLM at high temperatures usually has oxygen concentrations far below solubility or the so-called oxygen controlled range for corrosion mitigation. If no protective coatings or pre-oxidation has been applied to apparatus built with steels, this could lead to rapid dissolution attack at high temperatures (above 500-550°C for 316L type austenitic steels, or T91 and HT-9 type of ferritic and martensitic steels (for the compositions of these steels, see Chapter 6). Such dissolution attacks may be even accelerated if oxygen is added while the dissolution already started by removing dissolved elements through oxidation in HLM. It is highly recommended that heating be carried out through planned stages during the initial start-up, or after insertion of fresh test specimens, so that protective oxidation can be initiated and established. Since many test apparatuses and loops are built with steels, such precaution is essential in maintaining integrity of containment and safety.
If in static tests at high temperatures the oxygen concentration is not first adjusted to sufficient levels, due to the slow diffusion of oxygen from cover gas into the depths of stagnant HLM and rapid local consumption of oxygen by oxidation, unprotected fresh test specimens made of steels may start to dissolve, setting up a competition of mass transfer processes between oxygen diffusion to the steels and dissolution products migrating toward high oxygen areas (e.g. free surface in contact with cover gases). This could render test results highly dependent upon heating rate, initial oxygen concentrations in HLM and the effectiveness of the mass exchange from gas to liquid. It may even be dependent upon placement of specimens, size of surfaces and other system specific conditions, which are usually not accounted for or reported.

Such scenarios can also arise in flow systems where gas exchange for oxygen control is conducted through a stagnant volume. In extreme cases, it could lead to much more rapid corrosion than expected and have severe safety consequences.

**Gas injection**: This is often done to adjust coolant chemistry, either by adding oxygen or using hydrogen to reduce oxygen, or using gas mixtures (e.g. steam and hydrogen, or CO and CO₂) to maintain oxygen levels. Sometimes, to create circulation (e.g. gas lift or stirrer), a gas injection of high flow rate is applied.

It should be noted that even the highest purity supply gases usually contains ppm level of oxygen, which is too high for HLM if continuously applied over long periods of time. A getter system is needed to strip incoming gases of oxygen, unless adding oxygen is the goal. It is also not advisable to inject gases directly into HLM melt, since small amount of residual oxygen will lead to slag formation and plugging of the injection line, and the transport of slags to other parts may lead to flow restriction or blockage. This is true even for hydrogen injection unless an oxygen getter system, pre-heating to complete reaction with hydrogen, or entrainment by flow for prolonged hydrogen retention, is used.

From the safety perspective, injecting gases with lead oxide formation may create aerosols in the cover gas space, leading to potentially very hazardous conditions when opening and repair are conducted (see below on opening). It is therefore emphasised that cautions be applied when gas injection into liquid metal is deployed in experiments and operations.

**Cooling**: In the molten state, cooling should observe the same caution with heating. Rapid quench is not advisable.

The effects of cooling should be carefully considered when establishing procedures. Because solubility decreases with decreasing temperature, undesirable precipitation and deposition may occur in systems at hard to reach or technologically important sections. Once the solids deposit to walls, merely heating back up will not remove them since they either have low solubility or high melting temperatures. This could lead to reduced performance, restriction of flow and eventual blockage. It may also create unsafe conditions for maintenance and repair. The cleanup and restoration process can be very time consuming.

When temperature of HLM is lowered substantially from the operating conditions, oxygen concentration can reach saturation and precipitation will occur. Heating up quickly can lead to deficiency in oxygen for corrosion protection. For example, the typical oxygen control point is 10⁻⁶ wt.%, or 10 ppb of oxygen in LBE. This corresponds to approximately saturation at 200°C. So cooling below that for an extended period will lead to significantly lower oxygen concentrations, and addition of oxygen will be necessary on re-heating if the precipitated oxides are somehow removed of left out (e.g. cooling is in the melt tank).
Opening: As in all open vessel operations, this should be conducted at temperatures as low as possible. Lower temperatures suppress oxidation and vapour emission.

The top concern upon opening vessels or pipes is the potential presence and release of fine oxides or aerosols. While good ventilation is necessary, strong air perturbation at the openings should be avoided. When possible, a small enclosure of suitable sheets may be used to contain any releases. Operators should wear respirators if opening is carried out through cutting or other means of strong disturbances.

Extraction: It should be done at low temperatures. Very often, reheating is needed to extract specimens or sensors after solidifying HLM in place, or being “welded” to holders or sheaths by the residual HLM.

Cleaning: Cleaning of specimens is a difficult and delicate task. There are a number of methods reported for removing the adhered LBE from the specimens, including simple swiping, boiling in glycerine, silicon oil, or acid, or dipping in sodium. The safety precaution for each is obvious and will not be discussed here. One should keep in mind that hazardous waste is usually generated, as is also the case for polishing, and disposal needs to comply with applicable rules and regulations. Therefore, minimising the use of supplies and recycling of some media should be attempted.

It is also a good practice to clean up the surrounding areas after each opening or certain time, to reduce surface contamination and spread beyond the laboratory.

Freezing: While it is desirable to keep the HLM molten at all time, especially in test facilities, HLM will often be allowed to freeze. Due to volume changes upon solidification, and continued changes during recrystallisation in LBE, caution and proper procedures must be applied. Freezing should start at more confined space toward free surfaces, and should be avoided in regions where complex and/or delicate components lie.

An important consequence of the freezing is the reduction of oxygen in HLM. Upon melting, certain amount of time should be allowed for re-oxygenation before transferring and raising the temperature high.

For large test facilities, there are several additional steps or functions. The generic forms are transferring, priming, circulation, active cooling, draining, etc. The actual procedures will be facility specific. However, similar safety precautions are required. In particular, because of the stored kinetic and thermal energy in the circulating liquid metals, local containment in the forms of pipe cladding, loop enclosure, drainage collection floor pan, with ventilation, will be necessary.

The danger posed by lead to human health and environment is very real and serious, and should not be overlooked in the research and development of lead-alloy coolant technology. It is also demonstrated in the worldwide use of lead throughout the history that when rules and regulations are properly observed, and safe work practices and controls are employed and effectively utilised, lead hazards are manageable. It is imperative for this field of R&D and future applications that the safety guidelines are followed, and the workers and the environment are not harmed.
REFERENCES


NAAQS, US EPA:  [http://www.epa.gov/air/criteria.html](http://www.epa.gov/air/criteria.html)


Chapter 14

PERSPECTIVES AND R&D PRIORITIES OF HEAVY LIQUID METAL COOLANT TECHNOLOGIES*

14.1 Introduction

HLM technologies are being developed for a number of advanced nuclear systems. These include accelerator-driven transmutation systems to “burn” high-level nuclear waste and HLM-cooled fast reactors. Accelerator-driven systems are presently under investigation in Europe (EUROTRANS), South Korea (HYPER) and Japan (J-Parc). Pb/LBE-cooled fast reactors are one of the six concepts in the Generation IV Nuclear Energy Systems initiative. Different missions can be envisaged, where the more demanding missions include operating above 600°C for hydrogen production, or very long-life cores for non-traditional uses.

The most current knowledge of HLM technologies for applications below 600°C has been described in this handbook. Viewed from the perspective of programmatic applications for HLM technology and materials, there are a number of technological gaps to be filled before a prototypic test/demonstration nuclear system (reactor or ADS) can be designed, constructed and operated based on lead or LBE cooling. There are also a number of scientific issues which remain open, including fundamental physical, chemical and transport properties of HLM and materials, effects of environment, experimental and computational thermal hydraulics, coolant chemistry, measurement techniques and instrumentation. However, with the exception of uncertainties in materials performance over very long service life in cores (20 years or longer) at temperature over the 500-550°C range, no apparent conceptual barriers (i.e. “show-stoppers”) exist for the eventual use of lead and LBE coolants in advanced nuclear applications.

For applications in the higher temperature ranges an extensive R&D programme on materials and coolant technology is needed. But this is not yet foreseen at the international level. A preliminary analysis of existing materials led to the following classification, depending on the upper operating temperatures:

- **Class I.** For temperatures below 600°C, it has been demonstrated that the existing technologies and some code qualified nuclear structural materials (austenitic and ferritic/martensitic steels) possess acceptable performance in short to medium durations and out of pile. These demonstrations need to be extended to longer durations and under irradiation.

- **Class II.** For higher-temperature services envisioned in more advanced system concepts, materials and coolant technology developmental needs are much more extensive and the development much longer term. For reactor outlet temperature up to 650-700°C for higher efficiencies, ODS (oxide dispersion strengthened) steels and/or advanced F/M steels are potential candidates. These materials, categorised as Class II, may be used with an extension of the LBE coolant technology. For this temperature range, it is likely that Pb, rather than LBE, will be used, although the use of LBE is more established.

* Chapter leads: Concetta Fazio (FZK, Germany), Ning Li (LANL, USA).
• **Class III.** For operating temperature above 750-800°C in systems with more diverse energy products, including hydrogen production, refractory metal and alloys, ceramics and composites are potential candidates (Class III). These systems will require a very different coolant technology, and design, construction and operating methodology. Compatibility is no longer the key obstacle. Other issues, including irradiation stability, fatigue strength, fabrication, joint, costs, etc are challenging. The development of Class III materials are pursued by high temperature reactor and fusion technology development programmes. For this temperature range, Pb will likely be the only choice since LBE and the associated technologies no longer offer any intrinsic or experiential advantages.

14.2 Technology gaps, R&D needs and priorities for HLM systems operating at temperatures below 600°C

In Europe HLM technology is being developed mainly for the transmutation of high level nuclear waste in subcritical systems. The European project EUROTRANS, sponsored by the European Commission, aims to demonstrate the technical feasibility of transmutation of high level nuclear waste using accelerator-driven systems. Within this objective the design of an experimental facility (XT-ADS), should demonstrate the technical feasibilities: 1) to transmute a sizable amount of waste; 2) to safely operate an ADS. In addition, a conceptual design of the European Facility for Industrial Transmutation (EFIT) is also foreseen. The XT-ADS and the EFIT are subcritical reactor systems cooled by liquid lead-bismuth eutectic (LBE) and Pb, respectively. For both systems, a liquid metal neutron spallation target is the reference design basis for the external neutron source as driver.

The current XT-ADS and the EFIT design concepts foresee an outlet temperature for the HLM coolant no higher than 480°C and a maximum temperature of the fuel cladding at about 550°C under normal operating conditions.

Furthermore the European Lead-cooled System (ELSY) project has been outlined for the study in Europe of an about 600 MWe lead-cooled fast reactor. This project will be the European contribution to the LFR of the GenIV initiative and at present it is under evaluation at the European Commission for funding. The HLM technology specifications for ELSY will take advantages from the results coming out of the DEMETRA domain of the EUROTRANS project. However, some specific Pb technology developments have been foreseen as for instance high temperature materials characterisation in Pb and steam generator tube rupture studies.

In the US, HLM technology is developed in two advanced nuclear energy programmes: the Advanced Fuel Cycle Initiative (AFCI) and the GenIV Lead Fast Reactors (LFR). Within AFCI, there is no current system design effort. The basis is from the earlier concepts of accelerator-driven transmutation of waste, which are similar to EU’s ADS. Within GenIV LFR, while there are a range of envisioned missions and system concepts, the current focus is on a class of small- to medium-sized reactors with long-life cores (20 years or longer) and no on-site refuelling. The peak cladding temperatures in the design is limited to 650°C while core outlet temperature is approximately 560°C.

In Japan, there are several programmes developing HLM technology. The J-Parc has a transmutation component to design, build and test a LBE-cooled accelerator-driven transmutation system. A LBE spallation target demonstration is currently being pursued. The system conditions are similar to the EUROTRANS ADS concept. Other programmes are developing a range of concepts using HLM in advanced reactors or in intermediate heat exchangers, with conditions similar to or slightly less demanding than the US LFR specifications.
The situation in South Korea is similar, with HYPER (ADS) and PEACER (reactor) programmes developing HLM in collaborations with international partners. In particular, PEACER aims to design a low temperature LBE-cooled transmuter, well within the condition limits of other concepts.

14.2.1 HLM thermal-physical properties

This handbook contains most relevant thermal and physical properties of Pb, Bi and LBE with recommended correlations. For the high temperature range, a set of thermodynamic and transport properties (thermal conductivity, viscosity and surface tension) of LBE has been developed for use in the reactor safety analysis. However, due to a lack of experimental data published in the open literature, the basic properties such as the liquid density, vapour pressure and liquid adiabatic compressibility, were estimated up to the critical point using semi-empirical models based on the extrapolation of low temperature data of LBE or its constituents. A recommendation to produce experimental data in the high temperature range has been given, which would be of use to validate the computed values.

14.2.2 HLM chemical properties

The chemical properties data of solubility and diffusivity of oxygen and some metallic elements (e.g. Fe, Cr, spallation products as for instance Po, etc.) in the liquid metals and some oxides (e.g. iron oxides, chromium oxides, etc.) are of paramount importance for:

- the assessment of the materials corrosion rate;
- the design and engineering of HLM purification systems, for the development of a corrosion protection strategy that is based on protective oxide layers on the structural materials;
- the source term assessment.

A certain effort is needed to produce reliable solubility and diffusivity data.

14.2.3 Materials

The study of material properties changes in radiation environment, and specifically for HLM systems, the combined effects of radiation and corrosion, is a high priority R&D need. For instance the use of protective oxides as barriers against liquid metal corrosion may be compromised by radiation enhanced transport of ions in oxides, resulting in uncertainties for in-core components such as fuel cladding. In addition, there are insufficient modelling tools to analyse the varying test data and extrapolate the results to very long times, and only basic understanding of the triggers and kinetics of corrosion processes with long incubation periods, such as breakaway oxidation at high temperatures.

In addition, nuclear grade materials manufacture, fabrication and qualification are gradually becoming high priority issues as the HLM technology moves out laboratory and into test and demonstration facilities.

In the case of ADS systems developed in Europe, reference structural materials have been selected. These are the T91 martensitic steel for the highly loaded parts (cladding, wrapper, spallation target structure) and the AISI 316L austenitic steel for the vessel and in-vessel components. In addition it has been agreed to characterise Fe-Al based coatings, which are envisaged as an alternative protection method to the oxide layers grow, for the fuel claddings.
For design concepts in other countries, similar materials are selected. For example, the reference materials for LFRs in the US are HT-9 (T91 as a slightly more developmental backup) and 316L. The Russians developed some special alloys with added Si content for HLM cooled reactors, most notably EP823.

For these materials the basic data on compatibility and mechanical property changes in the liquid metals are already available, mostly under out-of-pile conditions. However, for the specific design requirements the following data are needed with high priority:

- long-term corrosion behaviour of the steels and the coatings;
- corrosion tests in LBE with low oxygen concentration in order to verify the low limit of the recommended condition for oxygen control;
- studies on corrosion erosion and friction mechanism;
- development of mass transfer model using reliable solubility and diffusivity data and corrosion data also for non isothermal systems;
- mechanical behaviour of the structural materials and the corrosion protection barriers in a representative temperature-stress field and more specifically:
  - creep;
  - fatigue and creep-fatigue;
  - fracture mechanics;
  - creep and fatigue crack growth.

In addition a very high priority is placed on the assessment of mechanical properties in the liquid metal and under irradiation of the steels and coatings.

These properties need to be measured in the relevant ranges of temperature, neutron fluence, stresses and HLM flow velocity for the different components. At the present the European design group for the ADS system has yet to produce a complete set of specifications to identify the testing ranges. Nevertheless, preliminary designs have allowed the definition of two major irradiation experiments in LBE in the HFR and BR2 reactors. These irradiation experiments will be performed in the temperature range of 350-550°C up to 4.5 dpa. Parallel irradiation experiments on T91 and Fe-Al based coatings in a fast spectrum (Phénix) have also been foreseen. In this case the irradiation temperature is 400-530°C and a dose of about 70 dpa may be reached.

Finally, the need to define standard procedures to perform corrosion and mechanical tests has been clearly expressed. At the European level, the laboratories will work towards the definition of such standard procedures.

After the completion of this materials testing programme, which performs a general assessment of the austenitic and ferritic/martensitic steels in LBE and under irradiation, the next step will be the performance assessment of manufactured materials in well defined shapes, e.g. tubing as fuel cladding.

14.2.4 Technologies

While much progress has been made in understanding the effect of coolant chemistry on materials corrosion, and measurement and control of oxygen in HLM in laboratory and small to medium test facilities, there are significant needs in scaling up to large systems, in particular pool-type and/or
natural circulation systems. Oxygen sensors for higher temperatures, deep immersion in liquid metals, and enhanced robustness and reliability in plant-like environment requires continued improvement from the state of art. Oxygen control systems, filtration methods, and oxygen activity maintenance and restoration after drainage, cool-down, freeze and thaw, will need further development and testing. Alternative and/or expanded control ranges, coupled with materials development, are desirable. Most of these are technological issues, and their priorities range from high to medium, depending on specific concepts and programme development paths and time horizons.

In the EUROTRANS the priorities have been envisaged for the development of:

- HLM purification systems for the control of aerosols and slags, to be applied in large scale facilities.
- Reliable instrumentation (flow meters, pressure transducers, thermocouples, level sensors, pumps etc.) for the long-term operation of HLM facilities.
- Reliable oxygen control methods and monitoring systems. Different types of methods have been envisaged to set the oxygen content in the liquid metal, these methods are based on liquid/gas or liquid/solid exchange. The efficiency of these systems needs to be assessed in order to make a selection of the most reliable and easiest method to be implemented in a nuclear system.
- Optimisation of on-line oxygen sensors in order to raise their reliability to nuclear standards. Effort is needed in the definition of a calibration strategy and to enhance their long term performance and thermal shock resistance.
- Instrumentation for the in-service inspection and repair (ISIR). These instruments need to be tested and calibrated in a combined LBE and irradiation environment.

14.2.5 Thermal-hydraulics

There are two kinds of open issues in this area. The first is related to the fundamental nature of heavy liquid metals. There are some needs in developing and validating more suitable turbulent model(s) for computational thermal hydraulics, especially for complex geometries and critical components, e.g. high-power spallation target windows in ADS and core configuration.

The second type of issues are technological and mostly related to the nature of the HLM-cooled system design and operation. Using coolant chemistry control and surface protective oxide formation to mitigate steel corrosion have consequences in heat transfer performance, particular for long-term or in abnormal situations, such as build-up of oxides and high level of solid oxide particles. HLM-cooled nuclear reactors usually have open lattice configurations to reduce pumping power needs and enhance passive safety. Flow circulation methods, transients, flow stability and elimination of undesired instability are all important issues to be investigated.

In the frame of the EUROTRANS project several experimental activities have been defined to support the design of the spallation target and the subcritical core.

According to the present design choices, the priority has been put on a free surface experiment in water and LBE to support the windowless target design. This activity will be strongly supported by CFD calculations. The CFD group will in turn use the results from the experiments to improve the related physical models, and to evaluate and benchmark the CFD codes.
In the thermal-hydraulics studies related to flow characterisation in the core region of ADS, two experiments have been defined according to design requirements:

- A single fuel pin experiment to evaluate the heat transfer in turbulent conditions across a prototypic cladding under the prototypical ADS conditions. This experiment will be conducted in the TALL facility at KTH, Sweden.

- A fuel rod bundle experiment to analyse the thermal-hydraulics behaviour of fuel assemblies. The plan is to specifically instrument the test section for local measurement of temperature, velocity and integral flow rate. The fuel bundle experiment will be conducted at the THEADES facility of KALLA at FZK, Germany.

At the present, no experiments have been yet been planned to support the safety analysis of severe accident conditions. These experiments need to be planned as soon as the design definition becomes more mature.
# List of Contributors

## Chair
Concetta Fazio (FZK, Germany)

## Scientific secretary
Byung-Chan Na (OECD/NEA)

## Peer reviewers
- Hans Ulrich Borgstedt (Germany)
- Ronald Ballinger (MIT, USA)
- Christian Latge (CEA, France)
- Hiroji Katsuta (Japan)

## Chapter Leads and Contributors

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Lead and Contributors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 1 Introduction</td>
<td>Concetta Fazio (FZK, Germany)</td>
</tr>
<tr>
<td></td>
<td><strong>Contributor:</strong> Ning Li (LANL, USA)</td>
</tr>
<tr>
<td>Chapter 2 Thermophysical and Electric Properties</td>
<td>Gianluca Benamati (ENEA, Italy)</td>
</tr>
<tr>
<td></td>
<td>Vitaly Sobolev (SCK•CEN, Belgium)</td>
</tr>
<tr>
<td></td>
<td><strong>Contributors:</strong> Hamid Aït Abderrahim (SCK•CEN, Belgium)</td>
</tr>
<tr>
<td></td>
<td>Michael Flad (DTI GmbH, Germany)</td>
</tr>
<tr>
<td></td>
<td>Allessandro Gessi (ENEA, Italy)</td>
</tr>
<tr>
<td></td>
<td>Heike Glasbrenner (PSI, Switzerland)</td>
</tr>
<tr>
<td></td>
<td>Koji Morita (Kyushu University, Japan)</td>
</tr>
<tr>
<td></td>
<td>Giuseppe Palombarini (Università di Bologna, Italy)</td>
</tr>
<tr>
<td></td>
<td>Yuji Kurata (JAEA, Japan)</td>
</tr>
<tr>
<td></td>
<td>Robert Stieglitz (FZK, Germany)</td>
</tr>
<tr>
<td>Chapter 3 Thermodynamic Relationships and Chemistry</td>
<td>Anne Terlain (CEA, France)</td>
</tr>
<tr>
<td></td>
<td><strong>Contributors:</strong> Vitaly Sobolev (SCK•CEN, Belgium)</td>
</tr>
<tr>
<td></td>
<td>Jean-Louis Courouau (CEA, France)</td>
</tr>
<tr>
<td></td>
<td>Laure Martinelli (CEA, France)</td>
</tr>
<tr>
<td></td>
<td>P. Agostini (ENEA, Italy)</td>
</tr>
<tr>
<td></td>
<td>A. Ciampichetti (ENEA, Italy)</td>
</tr>
<tr>
<td></td>
<td>Ning Li (LANL, USA)</td>
</tr>
<tr>
<td></td>
<td>Heike Glasbrenner (PSI, Switzerland)</td>
</tr>
<tr>
<td>Chapter 4 Chemistry Control and Monitoring Systems</td>
<td>Jean-Louis Courouau (CEA, France)</td>
</tr>
</tbody>
</table>
MEMBERS OF THE WORKING GROUP

BELGIUM

SOBOLEV, Vitaly
SCK•CEN
Reactor Physics and MYRRHA Dept.
Boeretang 200
B-2400 Mol
Tel: +32 (0)14 33 2267
Fax: +32 (0)14 32 1529
Eml: vsobolev@sckcen.be

CZECH REPUBLIC

DOUBKOVA, Alena
Nuclear Research Institute Rez plc.
Husinec – Rez 130
Rez 250 68
Tel: +420 266 172 520
Fax:
Eml: dal@ujv.cz

FRANCE

COUROUAU, Jean-Louis
CEA-DEN-DER-STR-LCEP
CEA Cadarache
F-13108 Saint-Paul-lez-Durance cedex
Tel: +33 (0)4 42 25 32 66
Fax: +33 (0)4 42 25 72 87
Eml: jean-louis.courouau@cea.fr

GORSE-POMONTI, Dominique
Centre National de la Recherche Scientifique
Centre d’Études de Chimie Métallurgique
UPR 2801
15, rue Georges Urbain
F-94407 Vitry-sur-Seine Cedex
Tel: +33 (0)1 56 70 30 61
Fax: +33 (0)1 46 75 04 33
Eml: dominique.gorse@glvt-cnrs.fr

KIRCHNER, Thomas
École des Mines de Nantes
Dep. SUBATECH
4, rue Alfred Kastler
BP 20722
F-44307 Nantes Cedex 3
Tel: +33 (0)2 5185 8454
Fax: +33 (0)2 5185 8424
Eml: thomas.kirchner@subatech.in2p3.fr

LAFFONT, Guy
CEA-Cadarache
Nuclear Reactor Division
F-13108 Saint-Paul-lez-Durance Cedex
Tel: +33 (0)4 42 25 73 14
Fax: +33 (0)4 42 25 66 38
Eml: guy.laffont@cea.fr
LATGE, Christian  
Research Director (NEA LBE Handbook review)  
DED-SEP Bâtiment 352  
CEA Cadarache BP N°1  
F-13108 Saint-Paul-lez-Durance Cedex
Tel: +33 (0)4 42 25 44 71  
Fax: +33 (0)4 42 25 44 74  
Eml: LATGE@desdsud.cea.fr

SERRE, Ingrid  
Chargé de Recherche CNRS  
Laboratoire de Métallurgie Physique  
LMPGM UMR CNRS 8517  
Bâtiment C6  
F-59655 Villeneuve d’Ascq Cedex
Tel: +33 (0) 3 20 43 66 06  
Fax:  
Eml: ingrid.serre@univ-lille1.fr

TERLAIN, Anne  
CEA-Saclay  
DEN/DPC/SCCME  
F-91191 Gif-sur-Yvette Cedex
Tel: +33 1 69 08 16 18  
Fax: +33 1 69 08 15 86  
Eml: anne.terlain@cea.fr

VOGT, Jean-Bernard  
Université de Lille 1  
Cité Scientifique  
F-59650 Villeneuve d’Ascq Cedex
Tel:  
Fax:  
Eml: jean-bernard.vogt@univ-lille1.fr

GERMANY

BORGSTEDT, Hans Ulrich  
Albert-Schweitzer-St. 33  
D-76139 Karlsruhe  
Tel: +49 721 682902  
Fax: +49 721 682902  
Eml: CHBorgstedt@web.de

FAZIO, Concetta (Chair)  
Programme NUKLEAR  
Forschungszentrum Karlsruhe (FZK) GmbH  
Hermann von Helmholtz Platz 1  
D-76344 Eggenstein-Leopoldshafen  
Tel: +49 7247 82 5517  
Fax: +49 7247 82 5508  
Eml: concetta.fazio@nuklear.fzk.de

KNEBEL, Joachim U.  
Head of Programme NUKLEAR  
Forschungszentrum Karlsruhe GmbH  
Postfach 3640  
D-76021 Karlsruhe  
Tel: +49 7247 82 5510  
Fax: +49 7247 82 5508  
Eml: ipeurotrans.knebel@nuklear.fzk.de

MÜLLER, Georg  
Forschungszentrum Karlsruhe (FZK)/IHM  
P.O. Box 3640  
D-76021 Karlsruhe  
Tel: +49 7247 82 46 69  
Fax: +49 7247 82 22 56  
Eml: georg.mueller@ihm.fzk.de

STIEGLITZ, Robert  
FZK/JKET  
P.O. Box 3640, JKET  
D-76021 Karlsruhe  
Tel: +49 7247 82 3462  
Fax: +49 7247 82 6321  
Eml: robert.stieglitz@iket.fzk.de
ITALY

AIELLO, Antonio
ENEA Fusion Division – CR Brasimone
C.P. 1
I-40032 Camugnano Bologna
Tel: +39 0534 801380
Fax: +39 0534 801225
Eml: antonio.aiello@brasimone.enea.it

BENAMATI, Gianluca
Head of Project
ENEA CR Brasimone
I-40032 Camugnano Bologna
Tel: +39 0534 801423
Fax: +39 0534 801250
Eml: gianluca.benamati@brasimone.enea.it

JAPAN

KATSUTA, Hiroji
Nagaoka 3524-129, Ibaraki-machi
Ibaraki-ken, 311-3116
Tel: +81 29-292-6004
Fax: +81 29-292-6004
Eml: hiroji_katsuta@atox.co.jp

KURATA, Yuji
Nuclear Transmutation Group
Center for Neutron Science
Japan Atomic Energy Research Institute (JAERI)
Tokai-mura, Naka-gun, Ibaraki-ken 319-119
Tel: +81 29 282 5059
Fax: +81 29 282 6489
Eml: ykurata@popsvr.tokai.jaeri.go.jp

MORITA, Koji
Associate Professor
Institute of Environmental Systems
Graduate School of Engineering
Kyushu University
6-10-1 Hakozaki, Fukuoka 812-8581
Tel: +81 92 642 3788
Fax: +81 92 642 3788
Eml: morita@nucl.kyushu-u.ac.jp

TAKAHASHI, Minoru
Research Laboratory for Nuclear Reactors
Tokyo Institute of Technology
2-12-1, O-Okayama, Meguro-ku, Tokyo 152-8
Tel: +81 3-5734-2957
Fax: +81 3-5734-2959
Eml: mtakahas@nr.titech.ac.jp

KOREA (REPUBLIC OF)

HWANG, Il-Soon
Professor, Ph.D.
Dept. of Nuclear Engineering
Seoul National University
56-1, Shinlim-Dong, Gwanak-Ku
Seoul, 151-742
Tel: +82 2 880 7215
Fax: +82 2 3285 9600
Eml: hisline@snu.ac.kr

SONG, Tae-Yung
Korea Atomic Energy Research Institute
P.O. Box 105, Yuseong
Daejeon, 305-600
Tel: +82 42-868-8924
Fax: +82 42-868-2080
Eml: tysong@kaeri.re.kr
**SPAIN**

**GOMEZ BRICENO, Dolores**  
Materials Project Head  
CIEMAT  
Avda. Complutense, 22  
E-28040 Madrid  
Tel: +34 91-3466605  
Fax: +34 91-3466661  
Eml: lola.gomezbriceno@ciemat.es

**SOLER CRESPO, Laura**  
Technology Department  
CIEMAT  
Avda. Complutense 22  
E-28040 Madrid  
Tel: +34 91-3466631  
Fax: +34 91-3466661  
Eml: laura.soler@ciemat.es

**SWEDEN**

**SEHGAL, Bal Raj**  
Royal Institute of Technology (KTH)  
Division of Nuclear Power Safety  
33A Drottning Kristina Vag  
SE-10044 Stockholm  
Tel: +46 (8) 790 9252  
Fax: +46 (8) 790 9197 (sec 9196)  
Eml: bsehgal@safety.sci.kth.se

**SWITZERLAND**

**DAI, Yong**  
Paul Scherrer Institute (PSI)  
CH-5232 Villigen PSI  
Tel: +41 56 310 4171  
Fax: +41 56 310 4529  
Eml: yong.dai@psi.ch

**GLASBRENNER, Heike**  
Paul Scherrer Institute (PSI)  
CH-5232 Villigen PSI  
Tel: +41 56 310 4712  
Fax: +41 56 310 3131  
Eml: heike.glasbrenner@psi.ch

**GROESCHEL, Friederich**  
(Alternate TG Metal member)  
Paul Scherrer Institute  
CH-5232 Villigen PSI  
Tel: +41 56 310 21 96  
Fax: +41 56 310 3131  
Eml: friedrich.groeschel@psi.ch

**NEUHAUSEN, Jorg**  
Institut für Radio- und Umweltchemie  
Paul Scherrer Institut (PSI)  
CH-5232 Villigen PSI  
Tel: +41 56 310 2407  
Fax: +41 56 310 4435  
Eml: joerg.neuhausen@psi.ch
### UNITED STATES OF AMERICA

<table>
<thead>
<tr>
<th>Name</th>
<th>Tel:</th>
<th>Fax:</th>
<th>Eml:</th>
</tr>
</thead>
<tbody>
<tr>
<td>BALLINGER, Ronald</td>
<td>+1 617 253 5118</td>
<td>+1 617 253 0807</td>
<td><a href="mailto:hvymet@mit.edu">hvymet@mit.edu</a></td>
</tr>
<tr>
<td>MIT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>185 Albany Street</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NW22-117, Cambridge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>02139</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LI, Ning</td>
<td>+1 505 665 6677</td>
<td>+1 505 667 7443</td>
<td><a href="mailto:ningli@lanl.gov">ningli@lanl.gov</a></td>
</tr>
<tr>
<td>Project Leader</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Los Alamos National Laboratory</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P.O. Box 1663, MS H816</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>87545 Los Alamos, NM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PASAMEHMETOGLU, Kemal</td>
<td>+1 208 526 5305</td>
<td>+1 208-526-2930</td>
<td><a href="mailto:kemal.pasamehmeto@inl.gov">kemal.pasamehmeto@inl.gov</a></td>
</tr>
<tr>
<td>AFCI National Technical Director for Fuels</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idaho National Laboratory</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P.O. Box 1625, MS 3860</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Idaho Falls, ID 83415</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### International Organisations

<table>
<thead>
<tr>
<th>Name</th>
<th>Tel:</th>
<th>Fax:</th>
<th>Eml:</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA, Byung Chan (Secretary)</td>
<td>+33 (0)1 45 24 10 91</td>
<td>+33 (0)1 45 24 11 28</td>
<td><a href="mailto:na@nea.fr">na@nea.fr</a></td>
</tr>
<tr>
<td>Data Bank</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OECD Nuclear Energy Agency</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12, boulevard des Îles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-92130 Issy-les-Moulineaux</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>