Refractory Metal Cladding and Mo-alloy Development for Accident Tolerant Fuel

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Refractory Metals as Cladding Materials for Enhanced Accident Tolerance
Behavior of Fuel/Core Materials in Severe Accidents
Zr-alloys, Fe-based and Ni-based Alloys and UO₂

- Zr Exothermic Reaction
- Hydrogen Generation
- Cladding Embrittlement

- Control Rod/Blade Collapse
- Rod/Blade Collapse

- Core Melt

- Zr-alloy Melting?

- UO₂ Melting

- Rapid Zr Cladding Oxidation

- Zr Cladding Balloon & Burst

- Great for Normal Operations

- 290-345°C

- Pressure effect

- 800°C

- 1000-1200°C

- 1400-1500°C

- 1850°C

- 2200-2800°C

- eutectic

- 1850°C

- 1400-1500°C

- 1000-1200°C

- 800°C

- 290-345°C

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What Can Enhanced Accident Tolerance Achieve?

- Add coping time for plant to recover
- Reduce hydrogen generation rate
- Eliminate design base LOCA concerns
- *Enhance passive LWR designs?*
- Reduce post-SBO heat removal requirement to low flow rate water injection (few liters/sec)

Assumes PWR with 24 hr passive cooling post-shutdown, then SBO with water injection at 2.5 l/s
Refractory Metals

- W, Ta, Re, Mo, Os, and Nb have the highest melting temperatures among metals in the periodic table.
- Availability and neutronic absorption properties limit the viable candidates to Mo and Nb for use as bulk cladding.
- Industrial use of Mo is widespread
  - Annual production of Mo is ~ 250,000 t
  - Tool steel alloys to improve strength, hardness, and corrosion resistance.
- Nb availability is more limited geographically and quantitatively (63,000 metric t/yr).

![Molybdenum world production graph]

Source: USGS
## Candidate Advanced Cladding Materials:
### Ceramics, Refractory Metals, Fe-based Alloys

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Temp (°C)</th>
<th>Thermal Neutron Absorption, barns</th>
<th>Thermal Conductivity, W/m-K</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr alloys</td>
<td>~1800</td>
<td>~0.19</td>
<td>22</td>
<td>Weakens at ~750-800°C</td>
</tr>
<tr>
<td>Stainless Steels</td>
<td>~1400-1500</td>
<td>~2.6-2.8</td>
<td>16</td>
<td>Fe-B eutectic melting at 1161°C; with Al addition resists steam to 1350°C due to formation of Al₂O₃</td>
</tr>
<tr>
<td>Inconel/Ni alloy</td>
<td>~1400</td>
<td>~4.0-4.2</td>
<td></td>
<td>Yields activation Co-58 product</td>
</tr>
<tr>
<td>SiC</td>
<td>(2600)*</td>
<td>0.09</td>
<td>20 (composite)</td>
<td>Ceramic, brittle</td>
</tr>
<tr>
<td>Mo</td>
<td>2623</td>
<td>2.6</td>
<td>138</td>
<td>Vaporizes as MoO₃ under oxidizing conditions; stable in reducing conditions to 2000°C</td>
</tr>
<tr>
<td>Nb</td>
<td>2477</td>
<td>1.15</td>
<td>53</td>
<td>Limited supply; susceptible to hydriding</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>2715</td>
<td>2</td>
<td>2</td>
<td>Stable in steam to 1900°C</td>
</tr>
</tbody>
</table>

*sublimation

Viable candidate materials are limited: SiC, Mo, stainless steels, and materials that form protective surface coatings, i.e., Al₂O₃, ZrO₂, SiO₂ and Cr₂O₃
High Temperature Mechanical Properties of ATF Cladding Material Candidates

Tensile properties of ATF cladding candidate materials (after S. Zinkel)

<table>
<thead>
<tr>
<th>Material</th>
<th>300°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircaloy-4</td>
<td>270</td>
<td>nil</td>
</tr>
<tr>
<td>Stainless Steel 304</td>
<td>475</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Ferritic Martensitic Steel</td>
<td>480</td>
<td>&lt;10</td>
</tr>
<tr>
<td>SiC/SiC Composite</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Molybdenum alloys</td>
<td>400-570</td>
<td>200-300</td>
</tr>
</tbody>
</table>
Mo as Principal Refractory Metal Option for Cladding

- **Beneficial properties:**
  - Tensile and creep strength at 1000 - 1800 °C
  - High stability in reducing and inert environments to ~2000 °C
  - Fabricability into long, thin wall tubes
  - Suitable for welding (i.e., end caps)

- **Challenges for LWR fuel applications:**
  - Higher neutron absorption cross sections than Zr (cladding wall thickness needs to be reduced, i.e., <0.25 mm)
  - Reacts with high temperature steam (needs improvement/protection)
  - Susceptible to radiation embrittlement (needs further evaluation)
  - Industry infrastructure for Mo cladding not established
  - R&D needed to support industrial applications
Progress on Mo-alloy Cladding Feasibility Studies
EPRI Coated Mo-alloy Cladding Designs

• All metal cladding concept
  – High strength Mo-alloy as core material
  – Coating on outer surface
    • Zr-alloy, or
    • Al, Cr-containing stainless steel
  – Optional inner coating: Zr or Nb

• Anticipated properties
  – Under normal operations
    • Zr-alloy or (Cr, Al)-containing stainless steel is compatible with LWR coolants
  – In accidents at >1000°C
    • Maintain rod integrity
    • Zr completely forms “protective” ZrO$_2$ at >1000°C
    • FeCrAl forms thin protective Al$_2$O$_3$ /Cr$_2$O$_3$
Scope of Feasibility Study

- Fabrication of thin-wall Mo tubes: 0.2-0.25 mm (8-10 mil)
  - Process and mechanical property optimization

- Reliable coating of Zr-alloy or FeCrAl

- Characterizations of key properties
  - Corrosion resistance in LWR coolants
  - Oxidation resistance at 1000-1500°C
  - Welding
  - Chemical/mechanical stability of coating (inter-diffusion)
  - Mechanical and burst/creep properties

- Irradiation effects
  - Coolant compatibility and embrittlement resistance

- Analysis:
  - Neutronic property (MCNC/Lattice Codes)
  - Thermal-mechanical behavior (FALCON) – PCMI, RIA
  - Accident tolerance (MAAP/MELCOR)
Fabrication of Thin-Wall Mo-alloy Cladding (1)
Mo and Mo+(0.3-1.0%)La$_2$O$_3$ ODS

- Tubes dimensions
  - PWR and BWR OD dimensions, 0.2-0.25 mm wall
  - ~1.5 meter (5 ft) long tubes
  - Good straightness, uniform wall thickness

- 7 batches fabricated so far
  - Generation 1 tube (stress relief annealed)
    - For coating, corrosion/oxidation testing, and welding
  - Generation 2 tube (recrystallized)
    - UTS ~450 mpa (65 ksi), 8 - 10% elongation at 320°C
    - 8 - 12% axial tube elongation
Fabrication of Thin-Wall Mo-alloy Cladding (2)

- Generation 3 tube under development
  - Goal: Fine equiaxed grain structure
  - Modification of texture during processing
  - Induction heat treatment
  - Looking for improved mechanical properties

- Areva FOA scope in 2015
  - Includes generation 3 Mo-alloy tubes
  - Scheduled fabrication in Q2 or Q3
Mechanical Property Tests

- Tube tensile properties (Rhenium Alloy Co., PMT, AREVA)
  - Room temperature, 320 °C
- Diametral tensile and creep properties (GE-GRC, AREVA)
  - Temperatures up to 1000 °C

Preliminary Results

Rod internal pressure at 600°C
- PWR ~727 psi
- BWR ~428 psi

Failure Strength 48 Ksi vs 17 Ksi for Zircaloy
(331 Mpa vs 120 Mpa)
Coating of Mo-alloy Tubes (via Deposition)

- Successful coating of Mo tubes and sheets
  - Physical vapor deposition (PVD) (CA-, EB-, DVD)
  - HVOF, HVAF spray
  - Vacuum plasma spray (VPS)

- Process parameters optimized
  - Good bonding
  - Good coating density
  - Good interface structure
  - Good uniformity
  - Good stability in autoclave at ~300 °C and in steam at 1000 °C

- Length of coated samples
  - 8-10” tubes
  - 36” tube

- Expensive, not conducive to scale up
Coating of Mo-alloy Tubes (by Mechanical Co-reduction)

- Goal: Demonstrate a more feasible process for commercial production
  - Economics
  - Quality control

- Based on prior work
  - Zircaloy tubes with Zr-liner (3 mil) on ID for BWR fuel cladding
  - Low Sn-Fe Zr alloy coating (3 mil) on Zircaloy-4 for PWR fuel cladding
  - Stainless steel coated Nb and Ta tubes in 1960s

- Mechanical co-reduction for Mo will be much more challenging
  - Hipping (bonding metal layers at high temperature under high gas pressure) will be used to form either mechanical or metallurgical bonds
  - Warm mechanical co-reduction (>300 °C)
  - Work planned for 2015
Tube to Plug Welding

- Successful with:
  - Plasma Welding
  - TIG (GTAW)
  - Electron Beam (EB) welding (ORNL, EBTec)
- EB welding employed for ATR rodlets
- Resistance projection welding feasible but needs development

Electron Beam Welding
(ORNL/EBtec)
ATR Rodlets (Richard Howard, ORNL)

Pass pressure test:
~2800psi (19 Mpa)
Reproducible

Resistance Projection Welding
(Solid State) - EWI

Appears feasible
Oxidation Resistance in 1000 °C Steam (Bare and Coated Mo Tubes)

- Large test chamber
- Feedwater de-aerated by purging with Ar gas
- Flowrate: 2.5 cc/min
- Test for 1 - 7 days
- ~10 tests performed
Oxidation of Sealed Tubes at 1000 °C for 3 and 7 Days
Steam, Steam + 10% Oxygen, Steam +10% Hydrogen

<table>
<thead>
<tr>
<th>Test Specimen</th>
<th>Before Test</th>
<th>10% H₂ Steam at 1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3 Days</td>
</tr>
<tr>
<td>PM Mo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCAC Mo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoLa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVD - Zircaloy 2 Coating</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>PVD - FeCrAl Coating</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HVAF - Zircaloy 2 Coating</td>
<td>**</td>
<td></td>
</tr>
<tr>
<td>HVAF - FeCrAl Coating</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Zr-2 coated
FeCrAl Coated
Zr-4 coated

~8 cm long sealed tubes

7 Day Test
3 Day Test
Oxidation of Coated Mo Tubes at 1000 °C

Mo tube with ~50 µm coating of Zircaloy-2

Before test

~50 µm Zircaloy-2

~200 µm Mo

After test

~75 µm ZrO₂

1 day

3 days

130 µm Mo

4 days

Mo tube with ~80 µm coating of FeCrAl

Before test

~80 µm FeCrAl

Before test – 4 days

FeCrAl

thin Al₂O₃

After test

Inter-diffusion layer thickness

• 1000°C
  - 1 day: 2 µm
  - 3 day: 4 µm
  - 7 day: 5 µm

• 1200°C
  - 1 day: 20 µm

Interface

Fe-Cr-Al

Mo-Fe-Cr

Mo
Bare Mo Oxidation Rate in De-aerated Steam at 1000 °C

- Bare Mo oxidation rate at 1000 °C ~20 µm/day
  - <1% of Zr oxidation rate

Bare Mo Open Tubes
Oxidation in 1000°C steam 3 days:

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<th>Test Specimen</th>
<th>Before Test</th>
<th>10% H₂ Steam 3 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM Mo</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>LCAC Mo</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>MoLa</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

Graph showing weight loss over exposure time:
- Steam Test 1000°C, 2.5cc/min steam flow
- Specimen Dimension: 0.4”OD x 0.5”L x 8mil WT
- Appearance of pittings and holes on 3 day specimens
- All specimens completely dissolved after 4 days

3 day data: LCAC Mo tube end was damaged during cutting
Steam Oxidation Tests >1000 °C

- Cause of localized oxidation under evaluation
- Majority of tubes intact with little metal loss
- Additional testing at 1200 – 1500 °C (GE-GRC and AREVA – France) to be completed in 2/3Q 2015

1200 °C - 24 Hour Test at ORNL (Courtesy Kurt Terrani - Funded by DOE-FCRD)
Irradiation of Mo-alloy Cladding

- Participation in DOE funded ATR-1 irradiation
  - 4 rodlets (~10 cm long with 4% enriched UO$_2$) in inert He gas
  - UO$_2$ purchased from AREVA
  - Rodlet assembly at ORNL
  - Irradiation to start in May 2015

- Possible future irradiations
  - INL ATR-2 in PWR water loop in 2016
  - Halden Reactor Program irradiation to start in 2016
  - Compatibility of Mo with UO$_2$ Pellets
  - PIE of coupled Mo-UO$_2$ discs irradiated at 500-400 °C in Halden Reactor to 112 GWd/MTU (samples courtesy of Halden Project)
  - Data needed to determine need for inner protective layer
Challenges for Resolution in Next 1 - 2 Years

- Optimize processes for GEN3 tube fabrication of Mo and Mo-ODS (Gen-3 tubes)
  - Fine equiaxed grain structure with uniform properties
- Mechanical co-reduction of outer layers
- Steam oxidation tests at ≥1200 °C (to ~1500 °C)
- Mechanical property characterization
  - Diametral tensile, creep and burst tests
- Solid state welding via resistance projection process (including coated tubes)
- Irradiation tests for embrittlement resistance
- New Mo alloys or surface chemistry modifications to improve corrosion resistance
Path Forward

- EPRI is collaborating with AREVA on Mo-alloy cladding development under DOE ATF FOA Phase 1B funding with a scope on Mo-alloy cladding
- Los Alamos National Laboratory is preparing (with EPRI input) a Technology Implementation Plan on Mo Cladding Development for U.S. DOE
- EPRI is also supporting two university groups on DOE – NEUP funding calls related to “resistance welding of coated Mo cladding” and “Modelling of ATF cladding”
Research Team

Major technical contributors (outside of EPRI)

- Young Kim + +, GE-GRC: coating, testing, evaluation...
- Todd Leonhardt, Rhenium Alloy Co.: tube fabrication
- Peter Ring: Heat treatment, hipping
- Sam Armijo, Consultant

AREVA: Forward research collaboration (through DOE FOA Phase 1B funding)

Analysis:

- RT Chiang: Neutronics
- Frank Rahn, MAAP accident analysis (+Fauske)
- Joe Rashid: Fuel rod thermal-mechanical behavior analysis

Collaborators

- Stuard Maloy, Los Alamos National Laboratory: nano-grain size Mo alloy, oxidation,….
- Kristine Barratt, INL – ATR test manager
- Richard Howard/Kurt Terrani, Oak Ridge National Laboratory: ATR rodlet welding, 1200°C steam test,
- EWI: Welding
- Ross Luther, PMT (now Thermocore Materials Technology), new Mo alloys
- Wah Chang: Zr-alloy supply
- Peter Hosemann, U.C. Berkeley
- AREVA: fuel pellets for ATR irradiation rodlets, research teaming
- Brian Cockeram, Bettis Laboratory

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