# STUDY OF STEEL TESTS OF STATIC CORROSION EXPERIMENTS IN LIQUID METAL PB-BI

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## Abstract

We try to evaluate the possibility of maintaining the corrosion-resistance of a structural material under the operational temperature and flow velocity of the optimized HYPER (HYbrid Power Extraction Reactor)[1] cooling system. It was attempted to consider the control of the oxygen concentration in the range of 350~650°C. Currently, we are performing static corrosion tests with the oxygen contents of a reduced and $10^{-7}$~ $10^{-5}$ wt% atmospheres at the temperature of 600°C. The concentration was controlled by adjusting the $H_2$ and $H_2O$ vapor ratio. In this paper, we will show the result of the experiment performed under the reduced atmosphere with an exposure time up to 1500 hours. The corrosion of 316L is irregularly severe under the reduced atmosphere due to the solubility of the nickel at Pb and Pb-Bi. Also small amount of iron and chromium was dissolved near the surface. On the other hand, the T91 and HT9 maintained the corrosion-resistance under the same condition.

## Introduction

Transmutation technology is being developed for reducing the amount of long-lived nuclides in the spent fuel from nuclear power plants. HYPER is designed as an accelerator driven subcritical transmutation system which is being studied by KAERI(Korea Atomic Energy Research Institute). Lead-Bismuth (Pb-Bi) eutectic alloy was determined as a spallation target and coolant material of HYPER due to its high production rate of neutrons and its effective heat removal.

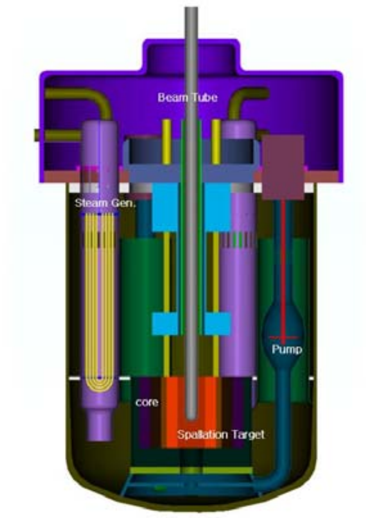
However, LBE has a great corrosion problem at high temperature. Thus, the problem has been considered as a important design-factor that limits the operational temperature and flow velocity of the ADS system [2][3].

In the past, several methods have been considered to prevent the corrosion problem in LBE. One of the methods is to control the oxygen concentration in the liquid LBE [4]. Thus, the corrosion behaviour can be reduced by forming a stable oxide layer on the material surface through an oxygen level control. Another one is to modify the surface of the material or the material compositions. Static corrosion tests are useful to investigate the corrosion properties and modes of various kinds of materials for developing the corrosion resistant materials.

KAERI finished the setup of the static corrosion facility in 2003, and started a static corrosion test and systematic research to develop the measuring techniques for the control of the oxygen concentration.

Figure 1 shows the conceptional layout of the HYPER system schematically. LBE is the target coolant material. The beam window material is 9Cr-steel. It is an advanced ferritic-martensitic steel that is known to be more resistant to LBE corrosion than austenitic steels. It does not show a ductile-to-brittle transition temperature (DBTT) problem while being resistant to radiation damage [5].

Figure 1. **Conceptional layout of the HYPER system**



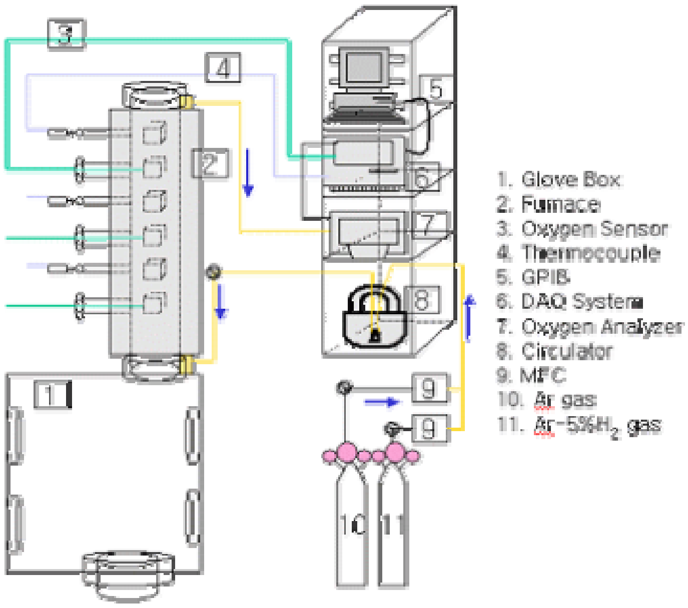
## Description of the static corrosion facility

Figure 2 shows the schematics of the static corrosion facility recently installed at KAERI. It is mainly composed of tube furnaces, a gas system and a glove box. The furnace discharges all the parts of the experiment, putting the specimen in Pb-Bi, which has a PID controller of a 3 Zone Type. It improves the reliability of the experiment by minimizing the temperature variation(±1°C) for each section along the test tube made of quartz with a 70mm inner diameter and 700mm length.

The rail and tray inside of the Quartz Tube make it possible to control the movements. Also, six crucible holes on the tray make it possible to measure the oxygen concentration directly and temperature of the Pb-Bi in each crucible. Each crucible was designed to put 4 in maximum at the same time, which has the advantage of obtaining reliable data. The dimension is 110 × 700(mm), the capacity is 10kw and the maximum operation temperature is 800°C. Because heated gas goes to the outlet during the experiment, a three stage heat filter was installed to protect the O-ring part from being heated.

In carrying out the corrosion experiment by controlling the oxygen, exposing the specimen to air causes contamination by oxidation. This is why we can't obtain reliable data. So a part of the furnace is linked to the glove box, which made it possible to start and finish the work in the glove box. The many intervals between them shows why it is hard to control the oxygen concentration and humidity if the glove box is affected by the high temperature of the furnace link. By attaching a cooling pan between them, room temperature can be maintained the middle of the experiment all the time. Separating the regenerator from the glove box protects it from the heated air, which goes into the regenerator, obstructs the oxygen absorption of Cu and brings the regenerator rate down. To heighten the reliability of the accurate data, the three sensors for the oxygen concentration measurement and the three holes for the thermocouple quartz were implemented.

Figure 2. **Schematics of the static corrosion facility**



The gas concentration of the furnace is monitored at the inlet and outlet position by the oxygen analyzing system of ZIPOX SMGT 1.6 up to an oxygen partial pressure of $10^{-21}\,ppm$. The temperature of the liquid metal Pb-Bi is measured by a K-type sheathed thermocouple in each crucible.

**The characteristics of the gas system**

Automatic changeover regulator is attached to the housing to supplying the gas continuously. Line regulator controls the high pressure of Ar-5%H2 and Ar gas. M.F.C (Mass Flow controller) of the Bronk-Host Hi-Tec and M.F.C Read out Unit are used to controll the gas flow amount by the reduced pressure. Fig. 3 shows a part of the gas system for the static corrosion facility. Pure Ar and Ar +5%$H_2$ gases are used. An automatic changeover and line regulator are attached to the housing which makes the handling safe and easy.

Figure 3. **Gas system of the KAERI static corrosion facility**

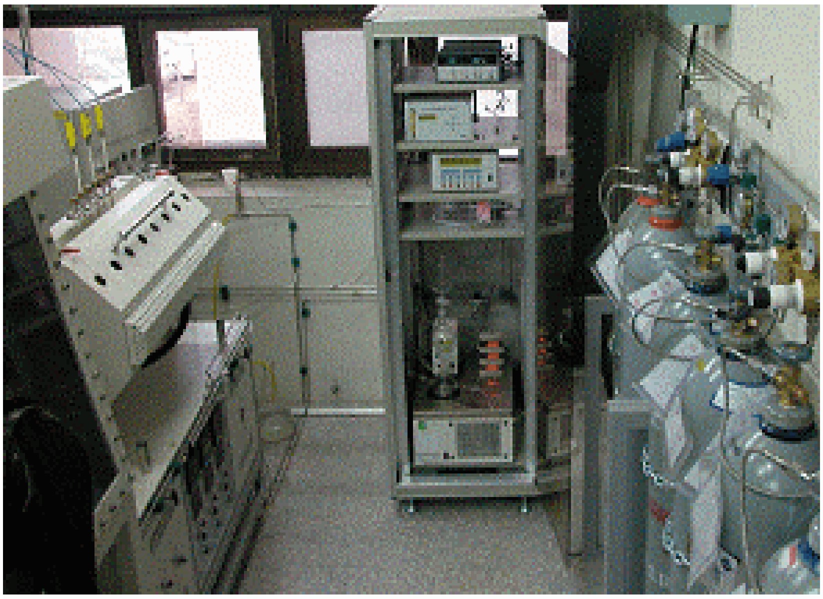
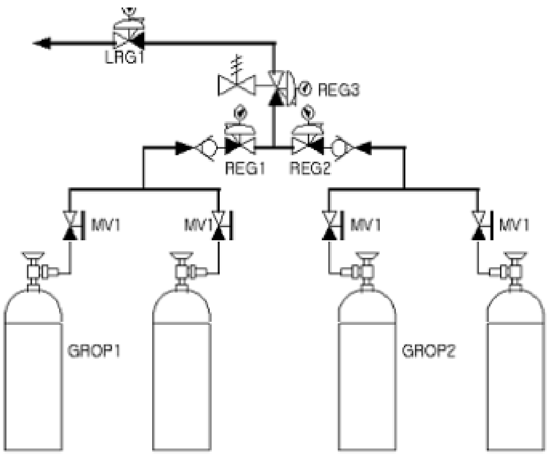


Figure 4 is the Schematics of the gas auto changeover system, which was designed for supplying gas safely and continually. Also, the user does not need to change the gas cylinder in supplying flammable gas or a poisonous gas. That means that an accident caused by a user's mistake can be prevented.

This system is divided into two groups with both sides having gas supplied from the gas cylinder. Each group is stood in a line. The supplying groups are always supplied by dividing them into two. When changing the gas container, all of the valves are operated. But when supplying, the valves are open.

Figure 4. **Schematics of gas auto changeover system**




Three parts of the REG are the most important things; the pressures in REG1 and REG2 are set differently from each other. KNOB part of REG2 makes a difference of about 2kg/cm$^2$ pressure than the REG1, which change the flowing direction of gas. For example, REG1 was set at a 10kg/cm$^2$ REG pressure and the gas is supplied. If the supply pressure falls to lower than 8km/cm$^2$, the gas flow is changed into REG2. During this time, from each REG, the check valve operates and obstructs the counter-current of the gas.

Oxygen analyzer SGMT1.6 ZIROX model is used with $2 \times 10^5 \sim 10^{-21}$ vppm in a sensor operating temperature of 750°C. Its measured voltage is 0~1500mV. Gas coming into the analyzer shows an accurate measured value when the range is 5~101/h.

**Experimental methods and procedure**

The test materials are 316L and some ferrite/martensitic steels such as HT9 and T91. The dimension of the samples is 10mm X 18mm X 2mm. And the samples were annealed at 1050°C for 1 hour and the heat treatment was done at 750°C for 2 hour except for the 316L. The test temperature was 600°C and the samples were exposed to Pb and Pb-Bi for 500~1500 hours. Table 1 shows the composition of the samples.

Table 1. **Chemical composition of specimens (wt%)**

| | **C** | **Si** | **Mn** | **Ni** | **Cr** | **Mo** | **V** | **Nb** | **W** | **P** | **S** | **N** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **HT9** | 0.19 | 0.36 | 0.59 | 0.53 | 11.79 | 0.99 | 0.31 | 0.02 | 0.49 | 0.019 | 0.006 | 〈 0.01 |
| **316L** | 0.02 | 0.35 | 1.8 | 12.1 | 17.3 | 2.31 | - | - | - | | | |
| ***T91*** | 0.105 | 0.43 | 0.38 | 0.13 | 8.26 | 0.95 | 0.20 | 0.075 | | | | |

The test was performed under reduced atmosphere. When a reduced atmosphere is needed, Ar-5% $H_2$ gas is forced to flow with a rate of 10cc/min for 7 days. Then the samples are put into the Pb-Bi and Pb for the corrosion test.

Total six crucibles were installed in the test tubes of the furnace and four samples were mounted in each crucible. The mass of the liquid metal Pb-Bi was around 55g for the corrosion test for each crucible of $Al_2O_3$, which was calculated by considering the volume, the solubility of the lead-alloy and the contacted surface between the samples and the lead-alloy.

The oxygen concentration was controlled by adjusting the $H_2$ and $H_2O$ vapour ratio. As an example, the oxygen concentration of $10^{-6}$wt% can be controlled by the chemical equilibrium between the Ar-5%$H_2$ and the water vapour [6]. Equations (1) ~ (4) are used to calculate the corresponding oxygen partial pressure. Then Equation (5) is used to determine the pressure ratio of $H_2$ and $H_2O$. The $H_2O$ pressure is set to be 15.94mbr. Ar gas is forced to flow with a rate of 100cc/min and the corresponding rate of the Ar-5%H2 gas is also forced to flow with the rate of 5ml/min.

$$a_0 = \frac{C_0}{C_0^*} = \left(\frac{P_{O_2}}{P_{O_2}^*}\right)^{1/2} \quad (1)$$

$$\log C_0^* = 1.2 - \frac{3400}{T} \quad (2)$$

$$\log P_{O_2}^* = 10.55 - \frac{23060}{T} \quad (3)$$

$$\log P_{O_2} = 2\log C_0 + 8.16 - \frac{16261}{T} \quad (4)$$

$$P_{O_2} = \frac{P_{H_20}^2}{P_{H_2}^2}\exp\left(\frac{2\Delta G_{H_2O}}{RT}\right) \quad (5)$$

$C_0$ : Oxygen concentration (wt%)

$C_0^*$ : Solubility of oxygen in Pb-Bi

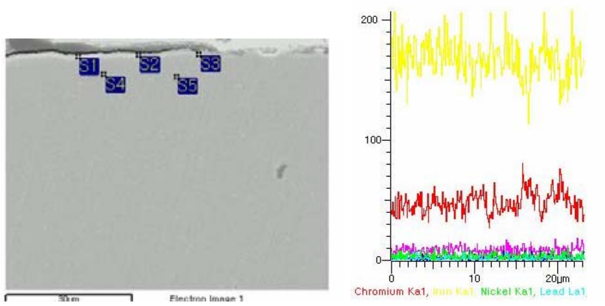
$P_{O_2}^*$ : Partial pressure saturated (bar)

T: Temp (K)

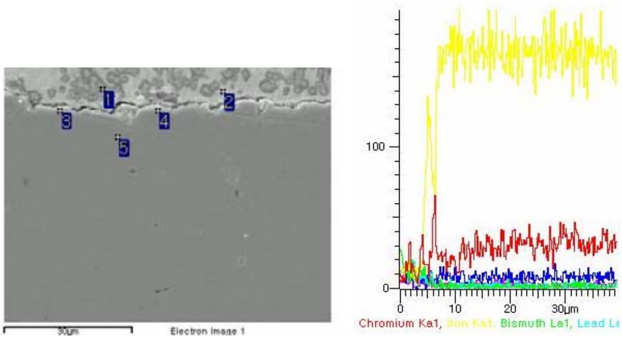
**Results and Discussion**

Figure 5 shows the EDX results of the T91 and HT-9 exposed to Pb-Bi at 600°C with the reduced oxygen content for 1500 hour. The oxygen meter shows that the oxygen content in the flowing gas is less than $10^{-8}$wt%. No dissolution attack was shown and the oxygen layer was not detected [3]. Also, when the T91 and HT-9 are exposed to Pb at 600°C, they have the same results as above.

Figure 5. **SEM/EDX of HT-9, T91 exposed to Pb-Bi at 600**°C **with oxygen content <$10^{-8}$wt%(1500h)**



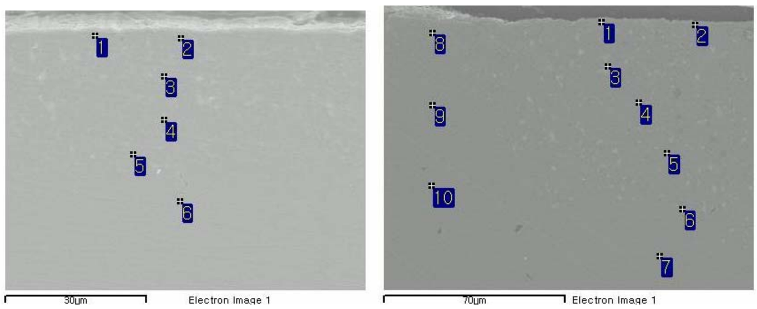

(a) HT9




(b) T91

Figure 6 shows the EDX results of the 316L exposed to Pb and Pb-Bi at 600°C with the reduced oxygen content for 1500 hour. The oxygen layer was not detected. Dissolution attack is clear and an EDX analysis was done for a part of the specimen. The corrosion shows a heterogeneous area through out the sample surface. The maximum depth of the dissolution is about 35 $\mu m$. Point 6 in Figure 6 (a) is located inside the specimen, so it is not affected by the Pb-Bi corrosion. Points 1 and 5 are located just below the surface and there is no Ni content in those regions. Instead, a small amount of Pb-Bi is attacked. Also, the result of the 316L exposed to Pb has the same corrosion problem as the case of Pb-Bi, which is shown in Figure 5 (b).

Figure 6. **The EDX results of the 316L exposed to Pb and Pb-Bi at 600℃ with the reduced oxygen content for 1500 hour**




(a) 316L at Pb-Bi (b) 316L at Pb

## Conclusions

KAERI built a static Pb-Bi corrosion test facility and performed experiments using it for a material screening and a systematic research to develop the technology for preventing corrosion. The solubility of Nickel is greater than that of Iron and Chromium in LBE. 316L austenitic steel has more Nickel than T91 and HT9 martensitic steel. Therefore the corrosion of 316L is severe under the reduced atmosphere due to the solubility of the Nickel. Also small amount of Iron and Chromium were dissolved near the surface.

## REFERENCE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