

Corrosion Characteristics of HT-9 in 500°C and 650°C Pb-Bi Liquid Metal

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The next generation nuclear power reactor will use Pb-Bi as the cooling material. The steel structure materials such as HT-9 used in the reactor suffer from corrosion when they are exposed to high temperature Pb-Bi. Therefore corrosion should be prevented to use Pb-Bi as the coolant material without any safety problem. One method is to control the oxygen content in Pb-Bi. An appropriate amount of oxygen in Pb-Bi can produce a thin oxide layer on steel, and this layer protects the steel from corrosion attack. Since the required oxygen content in Pb-Bi is in the range of 10^{-5} to 10^{-7} wt%, this small oxygen content can be controlled by flowing a mixture of hydrogen gas and water vapor. The stagnant corrosion test of HT-9 samples was performed by controlling the oxygen content up to 2,000 hours. The corrosion behavior of HT-9 was analyzed at the temperatures of 500°C and 650°C with a reduced condition and a oxygen content of 10^{-6} wt%.

Keywords : nuclear reactor, lead-bismuth, corrosion, oxygen control

1. Introduction

Korea produces 40% of its whole electricity by using nuclear power plants. Current nuclear reactors use water as a material to cool the nuclear fuel and generate electricity. One of the next generation nuclear reactors¹⁾ will use lead-bismuth (Pb-Bi) eutectic as a coolant material. Pb-Bi consists of 45% Pb and 55% Bi. Pb-Bi is solid at room temperature and its melting point is 125°C. Pb-Bi will be used as a liquid coolant in the next generation nuclear reactors since the working temperature range of Pb-Bi is higher than the melting point inside the reactor. Liquid Pb-Bi flows over the surface of the nuclear fuel rod to cool down the fuel rod. Pb-Bi contacts the fuel rod surface which is made of 12Cr steel HT-9. As the result of a cooling, the Pb-Bi itself can be heated up to a maximum of 650°C.

It is known that steels are damaged by Pb-Bi corrosion at such a high temperature. When steel is exposed to Pb-Bi at a high temperature, the components of the steel such as Fe, Cr and Ni are dissolved into the Pb-Bi to cause an integrity problem for the steel structure. It has been shown that corrosion attack can occur to about a 100 μ m depth from the surface for ferritic steel under the conditions of 575-750°C and 3,250 h of an exposure.²⁾

In general, the thickness of the fuel cladding is about 1 mm. The safety criterion for the cladding is that no more than 10% of the cladding thickness should be damaged for the lifetime of the cladding, which can be as long as a few years. Therefore, Pb-Bi corrosion can be a severe problem and we should develop the technology for preventing Pb-Bi corrosion.

One method is to form a stable oxide layer on the material through an oxygen control in Pb-Bi.³⁾ A mixture of hydrogen gas and water vapor produces a certain content of oxygen and the oxygen is dissolved in the liquid Pb-Bi. The dissolved oxygen reacts with steel and forms a thin oxide layer to protect the steel surface against Pb-Bi corrosion. Since the oxidation of metal surface is also another kind of corrosion, the oxide layer should be kept as thin as possible. It is important to establish the appropriate oxygen content to prevent Pb-Bi corrosion and the formation of a thick oxide layer.

Fig. 1 is the Ellingham diagram for some oxides.⁴⁾ The oxygen pressure of the atmosphere surrounding the Pb-Bi should be higher than the potential for Fe_3O_4 and lower than that for PbO. Then the oxygen dissolved in the Pb-Bi can produce the oxide layer on the steel surface while suppressing the formation of PbO, which can be an impurity in the Pb-Bi flow. PbO impurity can cause a blockage of the Pb-Bi path, which should be avoided.

We investigated the corrosion behavior of HT-9 in 650

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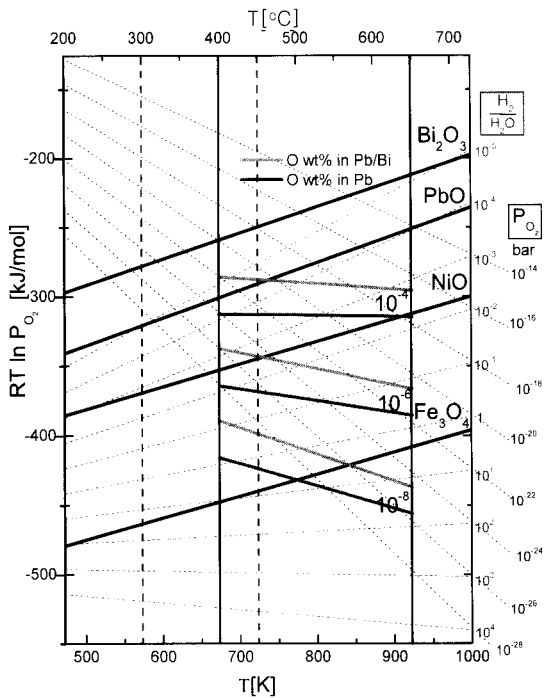


Fig. 1. The Ellingham diagram of some relevant oxides⁴⁾

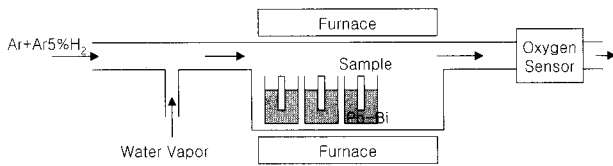


Fig. 2. Schematic layout of the stagnant corrosion test facility

°C liquid Pb-Bi and studied to see if the oxygen control method can be effective in preventing corrosion. We used the static corrosion test facility shown in Fig. 2 for the experiment. The motivation for the static corrosion experiment is to investigate the degree of corrosion damage for the materials due to dissolution by static Pb-Bi. Once a material is found to be stable under the static test, the next step is to study the corrosion damage due to the flowing Pb-Bi. If the materials pass the flowing Pb-Bi test, the final stage is to check the effects of radiation damage and the impurities in the material and Pb-Bi.

2. Experiment Procedure

Fig. 2 shows the layout of the Pb-Bi static corrosion test facility. Solid Pb-Bi is put into Al₂O₃ crucibles and heated to 500°C or 650°C where the Pb-Bi becomes liquid. Each crucible contains 32 g of Pb-Bi and it is located inside a quartz tube.

The tests were performed with two different oxygen contents. One is the reduced condition where the oxygen

content in Pb-Bi is less than 10⁻⁸ wt%. It is expected that an oxide layer will not be formed on the sample surface and the sample will be exposed to corrosion damage. When a reduced atmosphere is needed, Ar5%H₂ gas flow is maintained with a rate of 35 cm³/sec for 3 days. Then the samples are put into the Pb-Bi for the corrosion test.

The other oxygen content is chosen as 10⁻⁶ wt% since 10⁻⁶ wt% is between the potential for Fe₃O₄ and that for PbO in the temperature range of 400-650°C which is the working temperature range of the reactor. This can be seen from the Ellingham diagram in Fig. 1. The concentration does not vary although the temperature changes. If the oxygen concentration of 10⁻⁴ wt% is chosen, Fig. 1 shows that PbO is formed when the temperature decreases to 400°C. Therefore, 10⁻⁶ wt% is chosen as one of the concentrations applicable to the reactor system. We performed the test with the oxygen content of 10⁻⁶ wt% to investigate the formation of the oxide layer and the corrosion resistance by the oxide layer. When we control the oxygen content at 10⁻⁶ wt%, the corresponding oxygen pressure in the gas flow can be estimated based on Equation (1).

$$\frac{C}{C_s} = \left(\frac{P_{O_2}}{P_{O_{2,s}}} \right)^{\frac{1}{2}} \quad (1)$$

, where P and C are the pressure and concentration respectively. The values in the denominator are ones of a saturation state. C_s can be obtained from Equation (2).^{2),5)}

$$\log C_s = 1.2 - \frac{3400}{T} \quad (2)$$

, where C_s is the saturation concentration in wt%, and T is the temperature in K.

Ar, Ar5%H₂ and H₂O vapor are mixed to produce an oxygen content of 10⁻⁶ wt%. Once the needed oxygen pressure is determined, Equation (3) is used to determine the pressure ratio of H₂ and H₂O. The H₂O pressure is set at 15.94 mbar. Ar gas flow is set at a rate of 100 cm³/sec, and the corresponding rate of the Ar5%H₂ gas flow is also set.

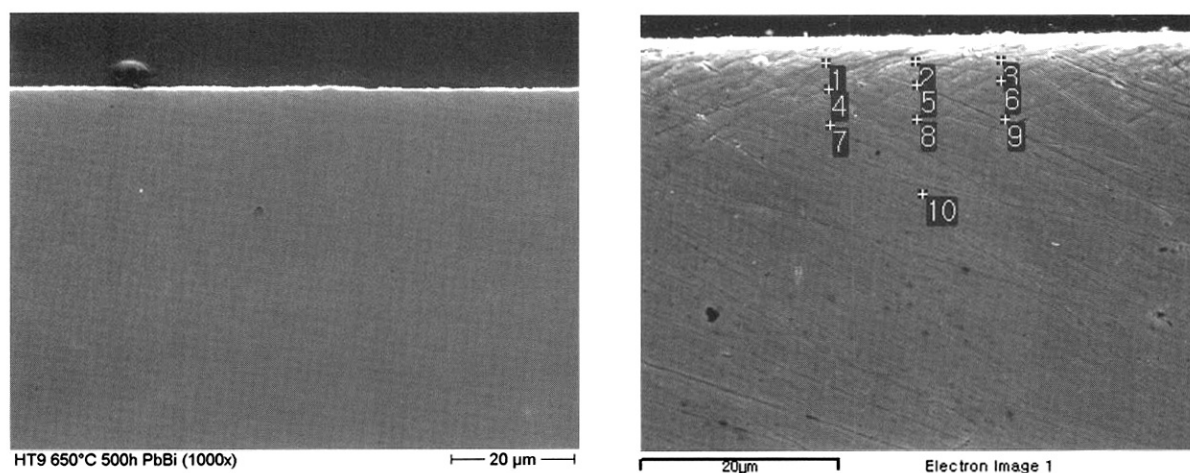
$$P_{O_2} = \frac{P_{H_2O}^2}{P_{H_2}^2} \exp\left(\frac{2\Delta G_{H_2O}}{RT}\right) \quad (3)$$

, where P and T are the pressure and temperature respectively.

The HT-9 samples are 2 mm thick and a heat treatment was implemented at 1,050°C for 1 hour and 750°C for 2 hours. Table 1 shows the atomic percentages of the components constituting HT-9. The maximum test time

Table 1. Chemical composition of HT-9 (atomic %)

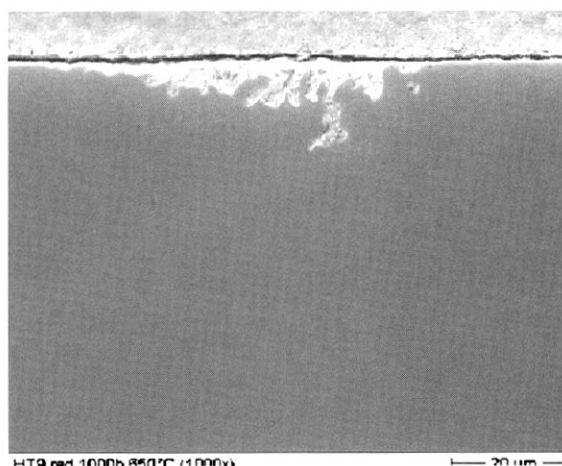
C	Si	Mn	Ni	Cr	Mo	V	Nb	W	P	S	N	Fe
0.19	0.36	0.59	0.53	11.8	0.99	0.31	0.02	0.49	0.02	0.006	<0.01	Bal.

**Fig. 3.** SEM results of HT-9 with reduced oxygen at 650°C (500h)

is 2,000 hours for the experiment.

3. Results and discussion

First, we analyzed a HT-9 sample which was exposed to 650°C Pb-Bi with a reduced condition. No clear corrosion attack was seen for the 500 h sample with the reduced oxygen content ($<10^{-8}$ wt%). Fig. 3 shows the clean surface of the HT-9. EDX analysis was also performed, and Table 2 lists the average atomic % of Fe and Cr for 3 points located at the same depth level. It shows that a small amount of Cr is dissolved near the surface. The atomic % of Cr inside the surface is increased compared to the value of original sample since we did not measure sample elements other than Fe and Cr. We continued the experiment up to 1,000 h. Fig. 4 is the result of the case of a 1,000 h exposure time. The corrosion attack is seen clearly, and the corrosion pattern is rather inhomogeneous.

**Fig. 4.** SEM results of HT-9 with reduced oxygen at 650°C (1000h)**Table 2. EDX results of HT-9 at points described in Fig. 3 (at. %)**

Point #	Fe	Cr	Pb	Bi	O
1-3	88.4	11.6	0.0	0.0	0.0
4-6	86.1	13.9	0.0	0.0	0.0
7-9	86.0	14.0	0.0	0.0	0.0
10	86.4	13.6	0.0	0.0	0.0
Original	87.8	12.2	0.0	0.0	0.0

The maximum depth of the corrosion is about 15 µm. EDX analysis was performed, and the results show that there is almost no Cr and Fe content in the spots where the corrosion occurred. It is known that Cr has a higher tendency to be dissolved in Pb-Bi than Fe.⁵⁾ The Cr content decreased to 4 - 5 at% in the region near the white region where the corrosion occurred. The Cr content is about 12 at% in the original HT-9 sample. That is somewhat related to the different solubilities of the components. The solubility of Fe, Cr and Ni are 12.1, 23.4 and 36,700 ppm respectively at 600°C Pb-Bi.⁵⁾ It was also observed that

Pb and Bi penetrated into the white region where the corrosion occurred. Bi has a higher tendency of penetration than Pb.

We also investigated corrosion at 650°C with a controlled oxygen content. Fig. 5 is the SEM pictures of the HT-9 exposed for 500 h with 10^{-6} wt% of oxygen. As can be seen in Fig. 5, the HT-9 of the 10^{-6} wt% case shows different characteristics from the case of the reduced Pb-Bi. When the oxygen content is 10^{-6} wt%, the corrosion is severe and the pattern is inhomogeneous. Fig. 5(a) is the pattern which can be seen most frequently. But there are some regions that have been attacked to greater depths by Pb-Bi, which is shown in Fig. 5(b). The greatest depth is about 120 μm and most of the Cr is depleted in that region. On the contrary, there are some regions where an oxide layer is formed and no Pb-Bi attack appears. Fig. 5(d) is one such region. Table 3 shows the EDX results at the points described in Fig. 5. Oxygen content was detected, unlike in the reduced case.

It was found that dissolution occurred in a short time

(1,000 h) at 650°C and an oxygen control of 10^{-6} wt% did not work properly to prevent a corrosion. That is because the dissolution activity of Pb-Bi is greater than the tendency of oxide formation at 650°C and 10^{-6} wt%.

The same experiment was performed at 500°C. Fig. 6 shows the structure of the sample exposed to the reduced Pb-Bi at 500°C for 2,000 h. There was no clear corrosion attack in this case although a small amount of Cr is dissolved into the surface.

Table 3. EDX results of HT-9 at points described in Fig. 5 (at. %)

Point #	Fe	Cr	Pb	Bi	O
(c)1	98	2	0	0	0
(c)2	42	2	11	10	35
(d)1	50	10	3	0	37
(d)2	80	10	0	0	10
(d)3	88	12	0	0	0

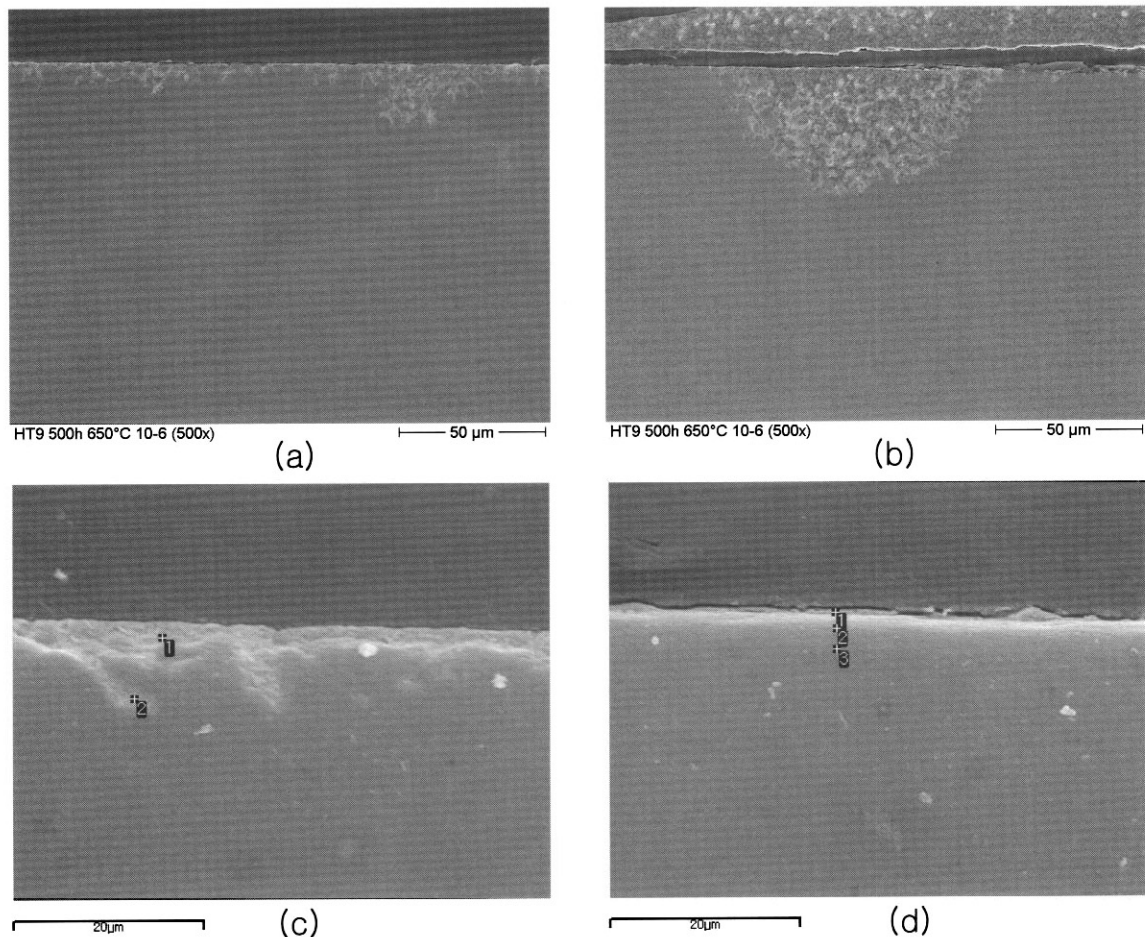


Fig. 5. SEM results of HT-9 with 10^{-6} wt% of oxygen at 650°C (500h)

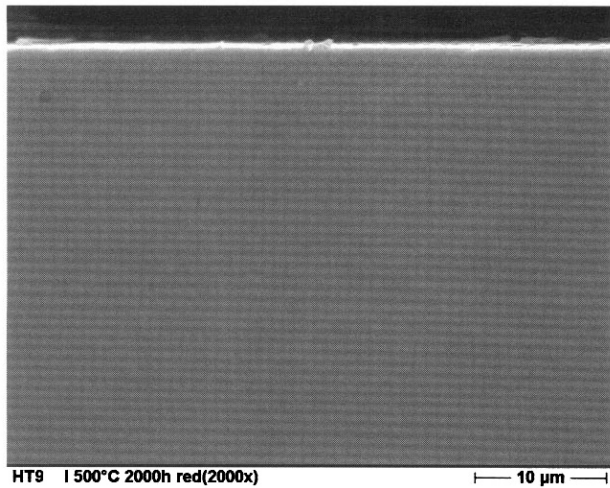


Fig. 6. SEM results of HT-9 with reduced oxygen at 500°C (2000h)

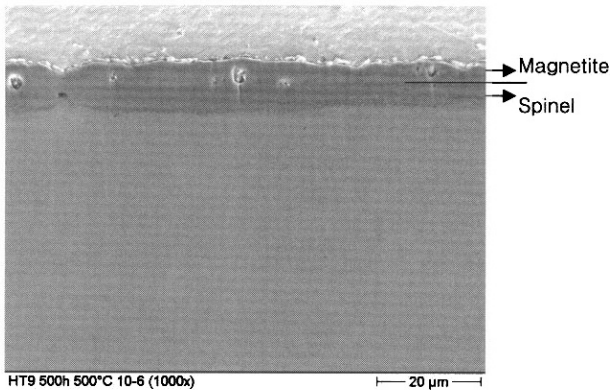


Fig. 7. HT-9 at 500°C with oxygen content of 10^{-6} wt% (500h)

The oxygen content is changed to 10^{-6} wt%. Fig. 7 is the result of the HT-9 exposed to Pb-Bi at 500°C with the oxygen content of 10^{-6} wt% for 500 h. The oxide layer consists of a magnetite scale and a spinel zone as expected. The thickness of each zone is about 6 µm. Atomic percent of the Fe varies from 40% to 60% and the oxygen from 30% to 40% in the magnetite scale. In the spinel zone,

Cr content is measured to be 13-16 atomic percent in addition to the Fe and oxygen contents.

In the case of 500°C, no clear corrosion occurred up to 2,000 h in a reduced condition, and the expected oxide layer was formed at an oxygen content of 10^{-6} wt%. Therefore, another exposure time test such as a one year test is needed to check on the corrosion resistance for a long time.

4. Conclusion

We performed stagnant corrosion tests of HT-9 with 500°C and 650°C Pb-Bi. When the test was performed with a reduced atmosphere (oxygen content $< 10^{-8}$ wt%) at 650°C, an inhomogeneous dissolution attack was observed for the sample. Although the oxygen content was changed to 10^{-6} wt% at 650°C, corrosion also occurred because the oxide layer was not formed successfully. In the case of 500°C, we did not see a clear corrosion attack with a reduced atmosphere up to 2,000 h. A firm oxide layer was formed when the oxygen content was changed to 10^{-6} wt% at 500°C. Therefore, corrosion can be a problem at 650°C, and the problem can not be solved by an oxygen content of 10^{-6} wt%. A longer exposure time test is needed for the 500°C case.

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