

Corrosion Behaviors of T91 Steel in Static Lead-Bismuth Eutectic

J. H. Choi, B. H. Choi, J. M. Kim, J. Y. Jeong, C. H. Cho(1), C. H. Cho(2) and B. H. Kim
Korea Atomic Energy Research Institute

1. Introduction

A new concept of a double tube bundle steam generator (DTBSG) system was proposed to eliminate a sodium water reaction (SWR) possibility in a sodium-cooled fast reactor, fundamentally [1]. The physico-chemical and nuclear characteristics of lead-bismuth eutectic (LBE) make this heavy liquid metal suitable to be used as an intermediate coolant in this system.

However, heavy liquid metals, and particularly LBE, present a high corrosivity to most of the structural materials. Martensitic steel has been proposed to be used as a steam generator (SG) tube material. Its compatibility with LBE in the operating conditions of this system depends on the formation of a protective layer such as an oxide film.

Martensitic steel T91 (Mod.9Cr-1M0) has been tested in LBE under static and isothermal conditions at 520 °C in order to gain the interaction between structural steel and the LBE, and to study the feasibility of forming and maintaining an oxide layer as a means of protecting the structural material.

2. Methods and Results

2.1 Test Apparatus

The static test apparatus is mainly composed of tube furnace, a glove box and a gas system.. Figure 1 shows a schematic diagram of a static corrosion test apparatus in liquid LBE.

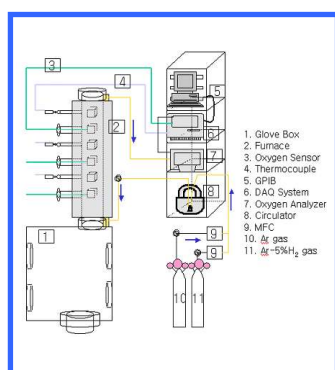


Fig. 1. Schematic diagram of the static test apparatus.

In the test at high oxygen concentration, as-received and aluminum-coated (60, 80, 100 μm thickness) specimens were used. The concentration of the furnace is monitored at the inlet and outlet position by the

oxygen analyzing system of ZIROX SMGT 1.6 up to an oxygen partial pressure of 10⁻²¹ ppm.

2.2 Oxygen Concentration

The chemical activity of oxygen in the lead alloy, however, is a critical parameter, because PbO precipitates if the activity is too high, and steel does not from a protective oxide layer if it is too low [2]. In terms of the Gibbs energies of formation of Fe₃O₄ and PbO, this condition is given by:

$$2\Delta_f G^\circ(\text{PbO}) > RT \ln p_{\text{O}_2} > 0.5\Delta_f G^\circ(\text{Fe}_3\text{O}_4) \quad (1)$$

where p_{O₂} gives the oxygen partial pressure in the gas atmosphere in equilibrium with the metal melt. The oxygen potential that is required to protect the steel surface by formation of stable oxide layers is here established by control of the H₂/H₂O ratio in the gas atmosphere above the LBE. The relation between the H₂/H₂O ratio and oxygen partial pressure is given by:

$$p_{\text{O}_2} = \frac{p_{\text{H}_2\text{O}}^2}{p_{\text{H}_2}^2} \exp \left(-\frac{2\Delta_f G^\circ(\text{H}_2\text{O})}{RT} \right) \quad (2)$$

2.3 Experiment

Two kinds of test were conducted at low oxygen concentration and at high oxygen concentration. For the test at low oxygen concentration, as-received samples only, and for the test at high oxygen concentration, as-received and aluminum-coated samples of T91 of 20 x10x2 mm, were tested in LBE at 520 °C for 500 and 1000 h.

The specimens were tested in porcelain crucibles containing approximately 100 g of LBE using a quartz tubing of 700 mm long and 70 mm internal diameter in the furnace. The test matrix is as shown in Table 1.

Table 1. The static test matrix

Oxygen concentration	Low	High		
Heavy liquid metal	LBE	LBE		
Test material	T91	T91	T91+Al. coating	
Coating thickness (μm)	-	-	60	80 100
Temperature (°C)	520	520		
Time (hr)	500, 1000	500, 1000		

To keep the oxidant potential of the LBE constant, a Ar + 4%H₂ gas flow of 30 cm³/min was continuously injected into the liquid metal. The enrichment of oxygen in the LBE was an oxygen activity of approximately 5.0 x 10⁻²³ wt%.

Figure 2 presents the SEM/EDX analysis of the samples tested with a low oxygen concentration at 520 °C. for 500 and 1000 h. As can be seen in Figure 2, in this environment, dissolution areas were not detected and the oxide layer was not formed on the surface.

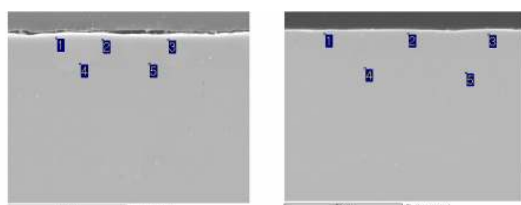


Fig. 2. SEM analysis of as-received T91 tested in LBE at 520 °C for 500 h (left photograph) and for 1000 h (right photograph).

Figure 3 shows the line analyses of the cross-section of T91 after corrosion tests in liquid LBE with a high oxygen concentration at 520 °C for 1000 h using SEM and EDX. Oxide layers with a thickness of around 5 μm formed on the as-received samples in several spots, but the oxide layer was not observed on the aluminum-coated samples. It is considered that the iron is easier to oxidize than the aluminum. The homogeneous dark grey aluminum-coated layers were presented as shown in Figure 2 (b), (c) and (d). In both of the as-received and aluminum-coated samples, dissolution areas were not detected. In the case of aluminum-coated samples, it seemed to contribute to protect the material.

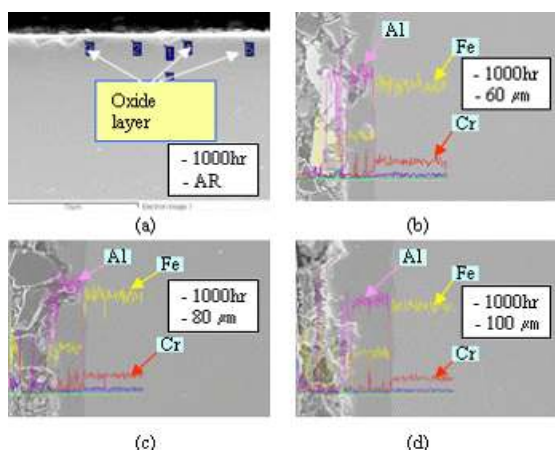


Fig. 3. SEM/EDX analysis of as-received (a) and aluminum-coated (b,c,d) specimens exposed to the LBE with an oxygen concentration of 5 x 10⁻²³ at 520 °C for 1000 h.

Figure 4 is an example of the results of EDX analysis for T91. In the corrosion tests under the condition of high oxygen concentration in liquid LBE, the double-layers composed of a Fe₃O₄ outer layer and a Cr-rich

spinel inner layer were observed. Corrosion attack by the liquid LBE was not so severe at 520 °C under the conditions of high and low oxygen concentrations. Therefore, it was considered that the formed Fe-Cr spinel oxide contributed to protect the material at 520 °C.

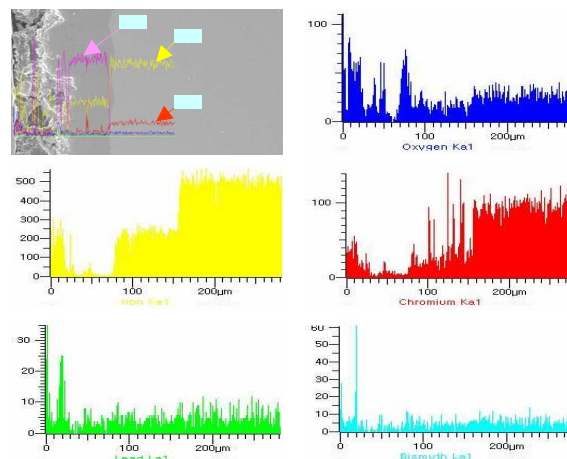


Fig. 4. EDX analysis of aluminum-coated specimen with a thickness of 100 μm exposed to the LBE with an oxygen concentration of 5 x 10⁻²³ at 520 °C for 1000 h.

3. Conclusions

In the low oxygen concentration conditions of martensitic steel T91, an oxide layer was not observed rightly, and dissolution areas were not detected. In the high oxidation conditions, the oxide layers were formed in the several spots on the as-received samples, but not formed on the aluminum-coated samples. It is considered that the iron is easier to oxidize than the aluminum. In both of the as-received and aluminum-coated samples, dissolution areas were not detected. In the case of aluminum-coated sample, it seemed to contribute to protect the material.

In the corrosion tests under the condition of high oxygen concentration in liquid LBE, the double-layers composed of a Fe₃O₄ outer layer and a Cr-rich spinel inner layer were observed. It was considered that the formed Fe-Cr spinel oxide contributed to protect the material at 520 °C.

Acknowledgement

This work was performed under ‘the Long-Term Nuclear Energy Research and Development Program’ sponsored by the Ministry of Education, Science and Technology of the Republic of Korea.

REFERENCES

- [1] Y. S. Sim and E. K. Kim, Characteristics of Integrated Steam Generators for Liquid Metal Reactor, J. of the KNS, Vol. 36, pp. 127-141 (2004).
- [2] G. Müller, G. Schumacher, F. Zimmermann, J. Nucl. Mater. 278 (2000) 85.