Corrosion Behaviors of T91 Steel in Flowing Lead-Bismuth Eutectic

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1. Introduction

In a sodium-cooled fast reactor (SFR), the possibility of a water/steam leak into the sodium in a steam generator and a violent sodium-water reaction (SWR) is indispensable. To resolve the SWR possibility in a SFR, a new concept of a double tube bundle steam generator (DTBSG) system was proposed [1]. The physicochemical 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. It's 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 flowing LBE under 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

Fig. 1 shows a schematic diagram of a flowing LBE test loop. The volume of the liquid LBE in the loop is 30ℓ . The circulation of the liquid metal is forced with an air-cooled electromagnetic pump.



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

The corrosion test specimen is an annular type with a diameter and a height of 10mm and 15mm, respectively.

The test specimen and the specimen support rod are linked together and installed in the vertical test section with a 3/4 inch diameter. The gap thickness between the test section and the test specimen is 5mm. The velocity of the liquid LBE is 2m/s. The oxygen concentration control of the loop was performed in the oxygen control tank by injecting the water vapor and hydrogen gases which passed through the circulator (constant temperature vessel). The oxygen concentration of the loop was analyzed by the released gases from the oxygen control tank by ZIROX SMGT 1.6.

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 Fe_3O_4 and PbO, this condition is given by:

$$2\Delta _{f}G^{o}(PbO) > RTlnp_{O2} > 0.5\Delta _{f}G^{o}(Fe_{3}O_{4})$$
(1)

where p_{02} 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:

$$PO2 = \frac{P_{H2O}^{2}}{P_{H2}^{2}} \frac{2\Delta fG^{o}(H_{2}O)}{RT}$$
(2)

2.3 Experiment

The corrosion test was performed in LBE at 520° C for 300, 500 and 1000 h. The circulation loop was heated up to 250° C, and the liquid LBE was charged from the sump tank into the loop by pressurizing the sump tank at about 0.3 MPa. Then, the LBE was circulated and heated up to the designated temperature. The test temperature was controlled in an isothermal condition at about 520° C by using the PID controller.

To keep the oxidant potential of the LBE constant, a $Ar + 4\%H_2$ 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 1.0 x 10⁻⁵ wt%.

For each exposure time, the cross-section of the specimen was rubbed with a cloth and analyzed by

means of scanning electron microscope (SEM) supplemented by qualitative energy-dispersive X-ray micro-analysis (EDX). The thickness of the scale on the steel surface was measured at 12 sites of the specimens in a light-microscope at a magnification of 1000X.

Fig. 2 presents the SEM/EDX analysis of the samples tested with an oxygen concentration of 1.05×10^{-5} wt% at 520 °C for 300 h. As can be seen in Fig. 2, in this environment, oxide layers were formed in several spots, but dissolution areas were not detected.





Fig. 3 is an example of the results of SEM/EDX analyses for T91 after corrosion tests in liquid LBE tested with an oxygen concentration of 1.05×10^{-5} wt% at 520°C for 500 h. Oxide layers were well formed on the surface with a thickness of around 5 μ m, and dissolution areas were not detected. In the corrosion tests, 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 sever at 520°C under these conditions of oxygen concentration and time. Therefore, it was considered that the formed Fe-Cr spinel oxide contributed to protect the material at 520°C.



Fig. 3. SEM/EDX results of T91 exposed to LBE with an oxygen concentration of 1.05×10^{-5} wt% at 520 °C for 500 h.

Fig. 4 shows the line analyses of the cross-section of T91 after corrosion tests in liquid LBE tested with an oxygen concentration of 1.05×10^{-5} wt% at 520°C for 1000 h using SEM and EDX. In this test also, oxide layers were well formed on the surface with a thickness of around 5 μ m, and dissolution areas were not detected.



Fig. 4. SEM analysis of T91 exposed to LBE with an oxygen concentration of 1.05×10^{-5} wt% at 520 °C for 1000 h.

3. Conclusions

In the case of all T91 specimens investigated after exposure at 520 °C in this test loop, oxides of Fe and/or Fe-Cr mixed-oxides formed on the steel surface and dissolution areas were not detected. In the corrosion tests under these conditions in liquid LBE, the doublelayers 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.

Additional experiments are necessary to confirm oxidation rates and investigate the time-dependence of oxidation under more controlled conditions with respect to the oxygen activity in the LBE.

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