

550 °C Liquid Lead-Bismuth Eutectic Corrosion of Direct Energy Deposited AFA Steel Laser Cladding

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1. Introduction

Nowadays, importance of small modular reactors(SMR) is highlight by their safety and carbon neutrality. Especially, nations having high popular density like Republic of Korea has advantage to use SMR due to their few or zero emergency planning zone(EPZ). Among the SMRs, Lead or Lead-Bismuth Eutectic(LBE) Fast Reactor type can solve spent nuclear fuel problem as generating more fissile material than consuming it. "The Future of the nuclear fuel cycle" also mentioned high safety and economics of the LFR [1]. However, corrosion problem of LFR has limited velocity and temperature of the coolant system. High solubility about structure material elements in the liquid lead can occur dissolution of main components like Fe and Ni, and then induce pitting corrosion or ferritization of substrate. To prevent the phenomena, various coating methods on the substrate have been developed. Direct Energy Deposition (DED) method shows better adhesion properties and faster fabrication than most other coating techniques. This advantage may be applied to a nuclear fuel cladding or a steam generator tube, which is a vulnerable part of a nuclear power plant, thereby increasing corrosion resistance of LFRs. This research studied LBE corrosion behavior of a DED laser clads, which applied a corrosion resistance material(Alumina-Forming Austenitic stainless steel; AFA) on STS316L plate(after called DED-AFA). STS316L plate clads manufactured by DED method(after called DED-316L) are immersed together to compare the corrosion behavior. Temperature and dissolved oxygen in LBE is 550 °C and 1×10^{-7} wt.%, respectively. After LBE corrosion for 500 hours, X-ray diffraction(XRD) analysis and Transmission Electron Microscope(TEM) analysis evaluate crystallography, microstructure and chemical composition of the oxide layers of both specimens.

2. Experiment

In this section, manufacturing process of both DED-AFA and DED-ST316L, LBE corrosion test and XRD, TEM analysis process are described.

2.1 DED Specimens Manufacturing

AFA and STS316L powder having ~100 μm diameter were used to stack clad layer with a thickness of about 0.5 mm on an STS316L substrate, respectively. AFA is corrosion resistance materials by forming alumina layer

on a corroded surface. To compare LBE corrosion performance of AFA, DED-316L specimens were manufactured. The plate specimens with a size of 10×12×2 mm were prepared for LBE corrosion test. The surface of each specimen was polished with SiC paper, diamond suspension, and 0.05 μm alumina colloidal solution. Thereafter, the plate specimens were sequentially cleaned at acetone, ethanol, and demi water for 3 minutes.

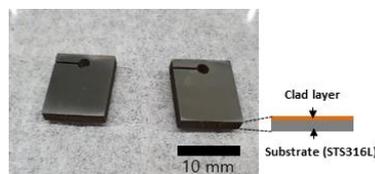


Fig. 1. DED-AFA and DED-316L specimens

2.2 LBE corroded sample preprocessing

Two types of specimens were corroded for 500 hours in a dissolved oxygen LBE environment at 550°C and 1×10^{-7} wt.%. After the test, the specimens were immersed in glycerin at 200°C to remove a residual LBE on the surface of the corroded specimen. In order to remove the remaining glycerin, ultrasonic washing was performed using acetone, ethanol, and demi water. Figure 3.6 shows the surface of the specimen from which the LBE has been removed.



Fig. 2. LBE corroded DED-AFA and DED-316L specimens

3. Results and Discussion

While alloys are corroded at LBE, an oxide film may be formed by bonding with oxygen on the alloy surface. Since the oxide film inhibits corrosion of the alloy by suppressing the dissolution of alloy elements and the penetration of oxygen into the alloy, it is necessary to analyze the mechanical behavior of the oxide film to evaluate corrosion performance. In the case of TEM, images can be measured at as high a magnification as possible up to the atomic unit, and are suitable for analyzing the behavior of nano-scale oxide films.

Furthermore, the composition of oxide films can be qualitatively measured using Energy Dispersive X-ray Spectroscopy (EDS).

2.4 TEM analysis

The oxide film cross-sectional TEM-EDS results of DED-AFA steel corroded for 500 hours at 550°C LBE are shown. An oxide film Fe_3O_4 and FeCr_2O_4 oxide film was formed with outer oxide on the surface of the specimen. On the other side, a thin and dense Al_2O_3 was produced in the internal oxide film, and Si oxide was also confirmed at the same position. Fe and Cr are contained in a large amount in the alloy and are produced as an oxide film outside the surface because of their high diffusion rate and low Gibbs free energy. On the other hand, the oxide of Al and Si, which is the most important for corrosion resistance, is stable due to a very low Gibbs energy, but is formed under an external oxide film due to a slow diffusion rate. Above all, the Al and Si oxide films can be easily formed, as Al and Si are protected by the external oxide film so that they can be formed as an oxide film with low diffusing to the outside. During 500 hours of corrosion, the AFA steel does not appear to have produced dissolution of Fe and Ni elements, except for Cr depletion for the formation of Cr oxide films near the surface.

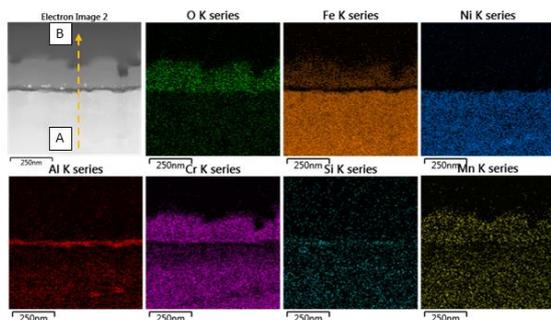


Fig. 3. TEM analysis of LBE corroded DED-AFA

The results of the oxide-film cross-section TEM-EDS of DED-316L steel corroded for 500 hours at 550°C LBE are shown. The outer oxide film is composed of Fe and Cr and is viewed as Fe_3O_4 or FeCr_2O_4 . A Cr oxide film was present in the inner oxide film, and a Si oxide film was also generated therein. While no Si oxide film was found during the corrosion of DED-316L steel in the previous studies, the DED manufacturing process seems to have provided an environment in which a Si oxide film could be generated. Although the Si oxide film was not dense in the corrosion experiment up to 2000 hours, it could not suppress the penetration of oxygen and the dissolution of alloy elements such as Fe, Cr, and Ni to the outside. Instead, it is shown that the Cr oxide film was densely formed with a high Cr content of about 18 wt.% to maintain considerable Ni inside the alloy compared to AFA steel. In addition, the $\text{Cr}_{0.52}\text{Fe}_{0.48}$ phase was locally formed, and the reason for formation is

believed to be due to the rearrangement of elements due to LBE penetration and ferritization due to Ni dissolution.

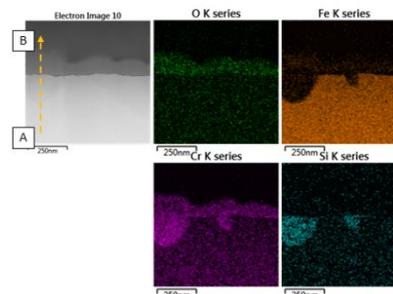


Fig. 4. TEM analysis of LBE corroded DED-316L

4. Conclusions

The corrosion performance of the clad materials which AFA and STS316L were manufactured by DED processing was evaluated. The oxide film behavior of specimens corroded for 500 hours was analyzed through TEM analysis, and all three alloys formed oxide films such as Fe_3O_4 , FeCr_2O_4 , or Cr_2O_3 as external oxide films. As an internal oxide film, which is important in corrosion resistance, Al_2O_3 was mainly densely produced in AFA steel by Al content, and Si oxide film was produced in the case of DED-316L. The Si oxide film of the DED-316L steel was not dense. For this reason, the DED-AFA also appear to have a low oxide film growth rate by suppressing oxygen penetration and alloy element dissolution through a dense oxide film. On the other hand, for DED-316L steel, it seems that the total oxide film thickness could increase because oxygen penetrates into the alloy and the alloy element dissolves outside. Nevertheless, the presence of a different Si oxide film and the thick internal oxide film create several barriers, which seem to have the same corrosion thickness as DED-AFA. This shows improved corrosion resistance compared to a general STS alloy, and it seems that the microstructure change caused by the DED manufacturing process could increase corrosion resistance by forming Si oxide film and other oxide film quickly in the early stages.

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