

Study on Alumina Forming Austenitic Stainless Steel exposed to 450 °C Lead-Bismuth Eutectic

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1. Introduction

Structural materials of 4th generation lead-cooled fast reactors show different corrosion behavior from those of light-water reactors due to properties of liquid metal like lead or lead-bismuth eutectic(LBE) like solubility and cohesiveness with the structure materials. Particularly, LBE has high solubility of Fe, Ni and Cr element which are main components in those structure materials, the structures can undergo severe dissolution. In addition, since LBE can contain a lot of dissolved oxygen, it can cause oxidation of the structure material rapidly. It is not possible to form a dense oxide layer like chromite in a LBE environment. Therefore, the porous oxide accelerates the dissolution problem more seriously [1].

Corrosion resistant materials for LBE environment are currently being developed and austenitic stainless steels are one of the candidate materials. Although general austenitic stainless steels do not form a sufficient oxide film to protect themselves, alumina forming austenitic(AFA) stainless steels including Al element can form a dense alumina oxide layer to improve corrosion resistance. The dense alumina oxide layer prevents penetration of oxygen diffused from LBE to the structural material and dissolution of alloy elements like Fe, Cr, and Ni included in the structural material. Therefore, AFA steels are possible to secure corrosion resistance superior to that of general austenite steel by preventing wall thinning of the structural material [2].

This study conducted LBE corrosion of SS316L and AFATi alloy. Through comparison between them, we researched corrosion behavior and mechanism of AFATi alloy. According to this study, we present the development direction of corrosion resistant AFA alloy design for LBE applications.

2. Experimental

2.1 Alloys

It is important to obtain passive layer for corrosion resistance in LBE. As Cr and Al elements in AFA alloy have lower Gibbs free energy than other Fe oxide layer, they help form stable oxide layers. Therefore, AFATi alloy developed in this experiment contain 13~20 wt.% Cr and 1~3 wt.% Al. And the content of Ni is 16~20 wt.% to maintain the austenite phase. Other minor elements are also added in AFATi alloy. Mo, Mn and Si element is for mechanical properties. Ti and C elements can enhance precipitation hardening and radiation resistance. Also, P

element is included for radiation resistance. In this experiment, corrosion behavior of AFATi alloy compared with SS316L. The chemical composition of alloys is described in Table I.

Table I: Chemical composition of the test alloys (wt.%)

	SS316L	AFATi
Fe	Bal.	Bal.
Cr	17.5	15
Ni	11.5	18
Mo	2.00	1.2
Mn	2.00	1.54
Si	1.00	0.38
Al	-	3
Ti	-	0.4
C	0.03	0.1
P	0.045	0.03

SS316L was fully-annealed at 1,050 °C Ar condition for 30 minutes. AFATi alloy was also annealed at 1,200 °C Ar condition for 2 hours, and then cold-worked from 2.63 mm to 2 mm thickness with 24 % reduction rate. Finally, the cold-worked AFATi alloy was recrystallized at 1,100 °C for 30 minutes and water-quenched. The test alloys were cut by electrical discharge machining to make 10×12×2t mm coupon specimens. The specimens were polished up to 0.05 μm alumina suspension step.

2.2 LBE corrosion test

Temperature and dissolved oxygen in LBE are main factors of material corrosion. Considering fuel cladding temperature of LFR system, LBE temperature in a corrosion test cell is 450 °C. Dissolved oxygen(DO) was maintained with 1×10^{-7} wt.% by using Ar mixed H₂ and O₂ gas. The oxygen concentration is optimum level to form Fe₃O₄ without PbO at 450 °C. AFATi and SS316L alloys were immersed for 500 hours in the 1 L static LBE cell. The temperature and oxygen concentration were monitored to check maintenance. Also, LBE chemistry was checked after the test and there is no change in chemical composition.

Oxide layer of the corroded three types of specimens were analyzed by using Transmission Electron Microscope(TEM) equipment with Energy-Dispersive X-ray Spectroscopy(EDS). Focused Ion Beam(FIB) equipment was used to make the TEM samples of the corroded specimens.

3. Results & Discussion

Fig. 1 shows severely corroded region of SS316L exposed to 450 °C, 1×10^{-7} wt.% DO LBE for 500 hours. Surface of the SS316L substrate is rough and double oxide layer on the SS316L substrate was formed. From the EDS results(Fig. 2) and diffraction pattern, upper oxide layer is magnetite(Fe_3O_4) and lower oxide layer Fe-Cr rich oxide which might be considered to Fe-Cr spinel. Thickness of the upper and lower oxide layers is 87.7 ± 18.6 nm and 33.3 ± 8.2 nm, respectively. LBE corrosion research about SS316L has been studied a lot and shows monolithic and mostly composed of Fe-Cr spinel at lower temperatures [3]. Similarly, most of surface of corroded SS316L in this test shows Fe-Cr rich oxide with 10 nm thickness. However, there is 20 nm porous Fe_3O_4 layer on the Fe-Cr rich oxide layer. Although Fe-Cr rich oxide layer can act as passive layer due to high Cr amount, it is not sufficient to prevent dissolution of alloy elements like Fe. Therefore, in the severely corroded region, the dissolution of Fe is accelerated, which occurs wall-thinning and thick outer Fe_3O_4 layer with rough surface like Fig. 1.

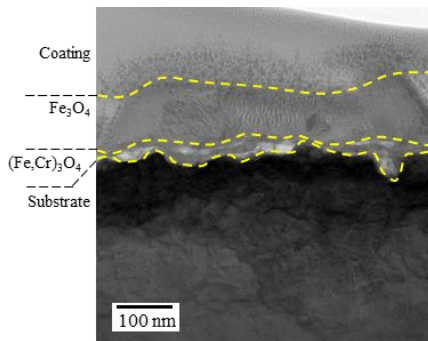


Fig. 1. BF-TEM image of SS316L exposed to 450 °C, 1×10^{-7} wt.% DO LBE for 500 hr.

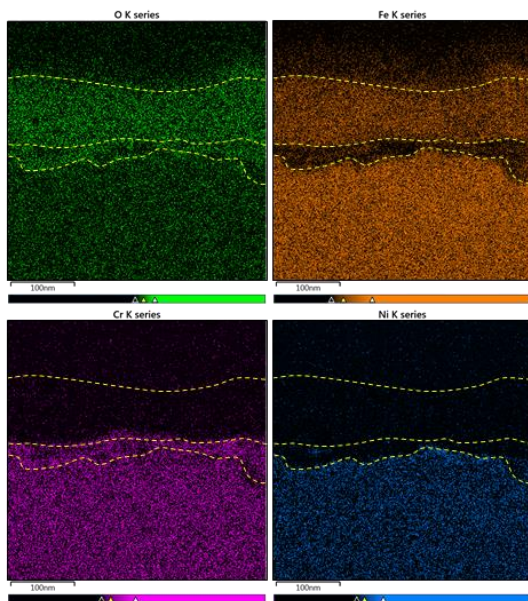


Fig. 2. EDS image of SS316L exposed to 450 °C, 1×10^{-7} wt.% DO LBE for 500 hr.

Fig. 3 shows cross-section of AFATi exposed to 450 °C, 1×10^{-7} wt.% DO LBE for 500 hours. Very thin oxide layer between outer oxide layer and the metal substrate was formed and a few pits in the oxide layer occurred. From the EDS results of AFATi(Fig. 4), the outer oxide layer is Fe oxide that seems to be magnetite, and interface oxide layer is Cr-Al rich oxide. The thickness of the outer oxide and the interface oxide is 33.8 ± 7.8 nm and 9.1 ± 1.3 nm, respectively. The AFATi alloy has lower Cr amount than SS316L. It means that AFATi alloy is harder to form passive Cr oxide layer than SS316L. Nevertheless, the AFATi alloy shows thin outer oxide layer and Cr-Al rich oxide layer. From the results, the Cr-Al rich oxide layer can inhibit diffusion of oxygen and alloy elements, effectively. And the Cr-Al rich oxide layer is uniform and thin with slow growth rate. The characteristic of slow growth prevents voids or pores inside the oxide layer. The slow growth of oxide layer seems to be affected by not only slow oxygen diffusion but also slow Al diffusion. However, there are some pits in the Cr-Al rich oxide layer. It is presumed that part of oxide has fallen off as the oxide layer grows since oxide layer under the pit has not been developed, rather than initial damage or corrosion. Pilling-Bedworth Ratio(PBR) means the ratio of cell volume of metal oxide to the cell volume of metal(Eq. 1). Density of $(\text{Cr}_2\text{O}_3, \text{Al}_2\text{O}_3)$ representing Cr-Al rich oxide is 4.33 g/cm^3 [4]. On the other hand, density of Fe_3O_4 and Fe-Cr spinel is 5.17 and 4.97 g/cm^3 [4]. Expansion of Cr-Al rich oxide having low density is larger than other oxides, which can occur oxide pilling. To mitigate the pilling of oxide, Diffusion of oxide elements like Cr and Al should be reduced. AFATi alloy has 0.4 wt.% Ti and 0.1 wt.% C to nucleate fine TiC precipitates which can increase diffusion rate of oxide element [5]. Therefore, Ti and C amount should be optimized to mitigate the oxide pilling and obtain oxide layer.

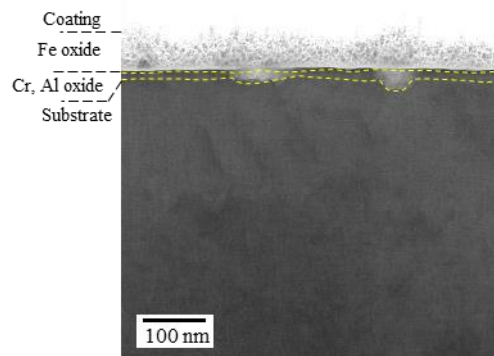


Fig. 3. BF-TEM image of AFATi exposed to 450 °C, 1×10^{-7} wt.% DO LBE for 500 hr.

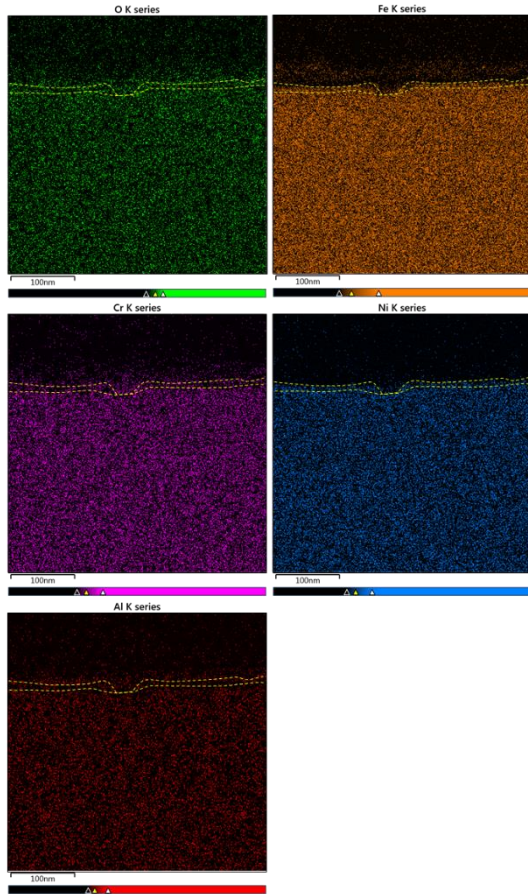


Fig. 4. EDS image of AFATi exposed to 450 °C, 1×10^{-7} wt.% DO LBE for 500 hr.

$$R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide} \cdot \rho_{metal}}{M_{metal} \cdot \rho_{oxide}} \quad (1)$$

4. Conclusions

Structure material applying for Lead/LBE fast reactor must survive in severe corrosion condition. Therefore, corrosion resistant materials like alumina-forming austenitic steels(AFA) have been developed. LBE corrosion test of SS316L and designed AFATi alloy conducted at 450 °C, 1×10^{-7} wt.% DO LBE for 500 hours.

1. The corroded SS316L having high Cr amount shows Fe-Cr rich oxide with 10 nm thickness. However, Fe_3O_4 oxide was also formed above Fe-

Cr rich oxide. It means that Fe-Cr rich oxide did not prevent diffusion of alloy elements sufficiently. Therefore, some region formed thick Fe_3O_4 outer oxide layer with 87.7 ± 18.6 nm thickness, and rough and porous Fe-Cr rich inner oxide with 33.3 ± 8.2 nm thickness.

2. The corroded AFATi alloy shows thinner oxide layers with 10 nm thickness. Interface Cr-Al rich oxide layer inhibited diffusion of oxygen and alloy elements. And slow growth of the oxide layer prevents voids or pores inside the oxide layer due to slow diffusion of oxygen and Al. However, there are some pits in the oxide because expansion of Cr-Al rich oxide layer is higher than other oxides. AFATi alloy has 0.4 wt.% Ti and 0.1 wt.% C to nucleate fine TiC precipitates which can increase diffusion rate of oxide element. Therefore, Ti and C amount should be optimized to mitigate the oxide pilling and obtain oxide layer.

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