Oxidation Behavior of Alumina-forming Duplex Stainless Steels in High Temperature Steam Environment

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1. Introduction

Since the Fukushima nuclear accident in 2011, considerable research on accident tolerance fuel (ATF) program has been conducted to provide larger safety margins from the current light water reactor (LWR) fuel systems [1]. Fe-base alloys, one of the candidate ATF cladding materials, showed good mechanical properties and oxidation resistance.

The iron-chromium-aluminum (FeCrAl) alloys have been used in many fields that need for high temperature oxidation resistance above 1000 °C. In view of the ATF cladding application, the oxidation resistance is mainly evaluated at LWR operating temperature and above 1200 °C, which is the criteria temperature of beyond design based accident (BDBA). Likewise, authors developed alumina-forming duplex stainless steels (ADSS) which showed excellent mechanical properties and oxidation resistance at LWR operating temperature and 1200 °C steam [2].

Though the maximum anticipated temperature in accident scenario is to be at 1200 °C, the cladding could also be exposed to the intermediate temperatures during the progress of accidents. So, ATF cladding is likely to be exposed to various temperatures below 1200 °C, the oxidation behaviors at such temperatures were not reported. Therefore, in this study, ADSS and FeCrAl alloys were exposed in pure steam environment at the various temperatures of 800 °C - 1050 °C and then the oxidation behavior of ADSS alloy was evaluated as compared to FeCrAl alloy.

2. Experimental methods

The chemical composition of tested materials was analyzed by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) method and the result is shown in Table 1. The ADSS (#B51) and commercial-grade FeCrAl (APM) alloys were machined into coupon-type specimens with diameter/thickness of 15/0.5 mm by electro-discharge machining (EDM) method. The coupon specimens were mechanically ground on both sides with 1200 grit SiC paper and ultrasonically cleaned in ethanol prior to the oxidation tests.

High temperature steam oxidation tests were performed at 800 °C, 900 °C and 1050 °C for 72 h. Distilled water with dissolved oxygen (DO) content below 100 ppb was supplied at a flow rate of 20 cc/min to the test chamber. Various analysis techniques such as weight change measurement, X-ray diffraction (XRD), scanning electron microscope (SEM) equipped with energy dispersive spectroscope (EDS) were utilized to analyze the oxidized specimens.

3. Results

The weight gains of ADSS#B51 and APM as a function of testing temperature are shown in Fig. 1. The degree of weight gains was very small in all tested alloys as compared to other non-alumina forming Fe-based alloys. Here, the weight gain of APM was similar at 900 °C and 1050 °C while it was lower at 800 °C. On the other hand, the weight gains of ADSS#B51 at 900 °C was higher than at 800 °C and 1050 °C. An increased weight gain at 1050 °C had been expected, yet the result of weight gain at 1050 °C was decreased from 900 °C. Such decrease was resulted from spallation of oxides during the cooling, which was later confirmed by the oxides analysis.

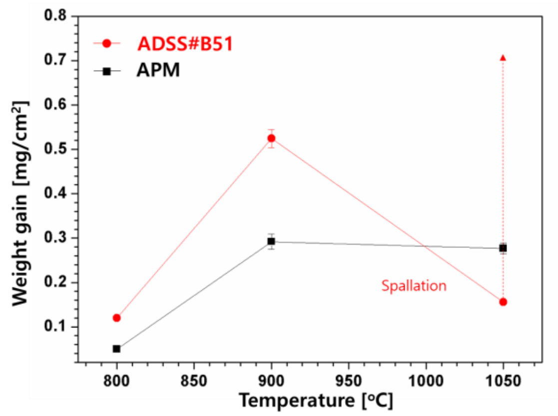

Fig. 1. Weight gain of ADSS alloy and APM after high temperature steam oxidation for 72 h.

Table I : Chemical composition of the ADSS alloy and a commercial FeCrAl Alloy

Composition[wt.%]	Fe	Cr	Al	Ni	Mn	Nb	Si	Ti	C	Remark
ADSS#B51	Bal.	16.33	6.14	18.77	1.04	0.53	0.31	-	0.11	Duplex + B2-NiAl
APM	Bal.	21.99	5.81	-	0.16	-	0.28	0.038	0.033	Ferritic

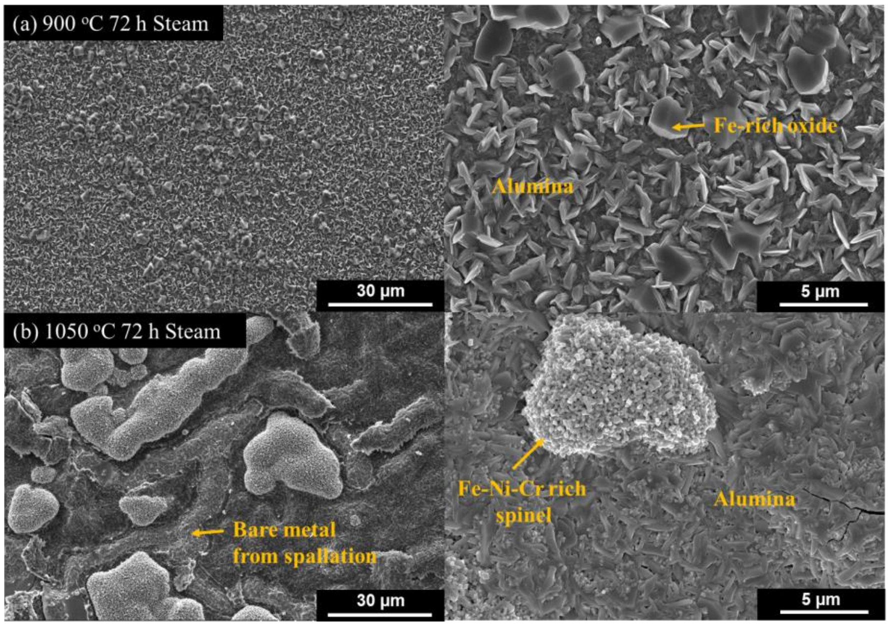

Fig. 2. SEM surface images of ADSS#B51 after steam oxdation at (a) 900 °C and (b) 1050 °C

Based on the weight gain results, surface oxide morphology was analyzed first and the results for ADSS alloy are shown in Fig. 2. At 900 °C, alumina was mainly observed along with nodular Fe rich oxides while a considerable area of bare metal was shown along with alumina and Fe-Ni-Cr rich spinel oxides at 1050 °C. Unlike the continuous surface condition after 900 °C, a large area of bare metal from spallation after 1050 °C may have caused the weight change drop. Without the spallation, a higher weight gain is expected (indicated as a dotted arrow line in Fig. 1) in consideration of the total thickness formed after 1050 °C.

A cross-sectional SEM image of ADSS alloy after 1050 °C was taken from the area with thick spinel oxides by focused ion beam (FIB) and EDS mapping as shown in Fig. 3. It was found that the surface Fe-Ni-Cr rich spinel oxide was formed about 3.5 μm thickness while a continuous alumina layer underneath the spinel had 1.8 μm thickness. The thickness of alumina after 1050 °C was similar to that of ADSS alloy after 900 °C. Therefore, it is reasonable to expect for the higher weight gain of 1050 °C since the thicker spinel oxide was formed with the similar alumina thickness as compared to that of 900 °C.

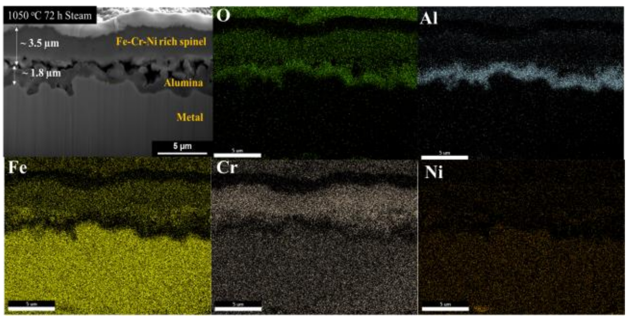

Fig. 3. Cross-sectional image by FIB and EDS mapping of ADSS#B51 after 1050 °C steam oxdiation

Summary

In this study, the oxidation resistance of ADSS (#B51) and FeCrAl (APM) alloys was evaluated at various temperatures in pure steam environment. Both alloys showed similar weight gains at 800 °C, while the weight change of ADSS was more sensitive to the testing temperatures than APM. Above 900 °C, ADSS alloy formed alumina with other surface oxides while APM formed only alumina layers. Despite the different oxide morphology between ADSS and FeCrAl alloys in the temperature range of 800 to 1050 °C, the weight gains were very small providing an excellent resistance to high temperature steam environment.

Acknowledgements

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