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Characterization of Alloy 600 joints exposed to a high-temperature supercritical-carbon dioxide environment

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ABSTRACT

Two types of Alloy 600 joints, such as diffusion-bonded joint and Alloy 182 fusion-weld, were exposed to supercritical-CO_2 environment at 550 and 650 °C (20 MPa) for 1000 h. The diffusion-bond region showed similar oxidation characteristics as parent Alloy 600, but the migration of diffusion bond line below oxide layer was observed due to the Cr-depletion induced recrystallization. For Alloy 182 fusion-weld, outer Mn-rich oxides (Mn_3O_4 and $MnCr_2O_4$) and a small amount of inner SiO_2 mixed with chromia were formed due to high Mn and Si contents. The presence of SiO_2 in chromia suppressed carburization at the oxide/matrix interface, which resulted in the formation of an amorphous C layer between the outer Mn-rich oxide and inner Cr-rich oxide. For Alloy 182 fusion-weld, tensile property changes after exposure to supercritical-CO_2 environment were negligible.

1. Introduction

Interest in the supercritical-carbon dioxide (S-CO_2) Brayton cycle energy conversion system has been raised as an alternative option for the conventional steam Rankine cycle [1–4]. By applying S-CO_2 cycle, improved thermal efficiency combined with compact-sized turbomachinery components could be achieved. The operating conditions of the S-CO_2 cycle would be dependent on the various applications (mostly temperature) such as Gen. IV nuclear reactors (500–850 °C), advanced-fossil plants (650–760 °C), and concentrated solar power (~800 °C) with pressure of 20–30 MPa [3,4]. In these systems, for high heat transfer efficiency, micro-channel type heat exchanger (HX) would likely be adopted as a key component where thermal energy from the heat source is transferred to S-CO_2 cycle [5].

For HX material selection, material compatibility in high temperature S-CO_2 conditions should be properly taken into account. Candidate materials are required to have good corrosion and carburization resistance to assure heat transfer capability and structural integrity. Therefore, S-CO_2 corrosion tests of various candidate materials have been conducted at the temperature ranges of 550–750 °C with pressures of 0.1–25 MPa [6–18]. According to these studies, it was generally observed that corrosion resistance of chromia (Cr_2O_3)-forming Fe-based alloys (21–25 wt% Cr) and Ni-based alloys (16–28 wt% Cr) was superior to Fe-rich oxide forming alloys. In addition, the authors have reported that despite the existence of a continuous chromia layer, an amorphous C layer was formed at the oxide/matrix interface as a result of carburization in S-CO_2 environment. However, further carburization in the underlying matrix (carbide formation) did not occur in Ni-based alloys because of superior carburization resistance [6].

Though most researches regarding high temperature S-CO_2 corrosion tests were conducted on base metals, for practical applications, joining is inevitable. For example, HXs would be fabricated by diffusion bonding of thin metal sheets with micro-channels [5]. In this case, the corrosion and carburization behavior along the diffusion bond line might be different from those of the base metal, which could act as weak points, deteriorating the integrity of HXs. Moreover, fusion-welding would be also used to join HXs with pipes and other components. However, the joints of candidate alloys, such as the diffusion-bond and fusion-weld, were rarely studied.

In this study, the corrosion and carburization behavior of chromia-forming Ni-based joints, i.e., diffusion-bonded and fusion-welded, were investigated after being exposed to a S-CO_2 environment at 550–650 °C (20 MPa) for 1000 h. Oxidation characteristics and its subsequent effect on carburization behavior at those joints were evaluated. Finally, the changes in tensile property after exposure to S-CO_2 environment were assessed.

2. Experimental Method

2.1. Materials and Specimen Preparations

Two joint types of Alloy 600, a wrought Ni-based alloy, were used in

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Table 1
Chemical compositions of chromia-forming Ni-based alloys used in this study (in wt%).

	Ni	Cr	Fe	C	Nb	Mn	Ti	Al	Si
Alloy 600 (diffusion-bond)	Bal.	16.1	9.3	0.08	–	0.3	0.2	0.2	0.3
Alloy 182 (fusion-weld)	Bal.	17.2	11.5	0.2	2.0	5.1	0.1	–	0.9

this study. That is, diffusion-bonded joint of Alloy 600 and fusion-weld using Alloy 182 filler metal were prepared. The chemical compositions of the Alloy 600 base metal and Alloy 182 fusion-weld metal were analyzed by inductively coupled plasma (ICP) method and the results are listed in Table 1. Alloy 600 was chosen for this study as it was reported to show good corrosion and carburization resistance in S-CO_2 environments at 550–650 °C and 0.1–20 MPa [6,8].

The diffusion bonding was conducted following the procedure previously developed by I. Sah et al. [19]. Prior to diffusion bonding, the surfaces of Alloy 600 blocks (20 mm × 20 mm in length and width and 10 mm in thickness) were ground with ANSI 1200 grit silicon carbide paper and ultrasonically cleaned in ethanol. Diffusion bonding was performed by TNP Corporation, Korea as follows. Two blocks were installed with the ground surfaces in contact, which were then heated in vacuum to 1040 °C and held for 10 min. Then, a pressure of 9 MPa was applied on the blocks for 1 h. After diffusion bonding, post bond heat treatment (PBHT) was performed in vacuum at 1010 °C for 20 h followed by air cooling to improve bonding efficiency [19]. Finally, the blocks were electro-discharge machined to mini-sized tensile specimens (16 mm in length and 0.5 mm in thickness) maintaining diffusion bond line at the center of the specimen.

Alloy 182 filler metal (ENiCr-3, 4.0 mm), which is commonly used as a fusion weld metal of Alloy 600, was used to prepare the single V-groove fusion-weld between the 40 mm-thick blocks of 316L stainless steel and SA508 low alloy steel by the shielded-metal arc welding (SMAW) process. During the welding process, voltage and ampere were kept at 140–160 A and 23–24 V, respectively, while the heat input rate at 11–23 kJ/min. Weld blocks were not post-weld heat treated. Corrosion coupons (10.5 mm in diameter and 1 mm in thickness) and mini-sized tensile specimens were electro-discharge machined from the fusion-weld region away from the fusion line. The loading direction of the tensile specimen was along the welding direction. Corrosion coupons were ground on both sides with 1200 grit silicon carbide paper and cleaned in ethanol prior to exposure to S-CO_2 while both surfaces of the mini-sized tensile specimens were lightly ground with the 800 grit paper before the S-CO_2 exposure.

Fig. 1a and b show surface electron backscatter diffraction (EBSD) inverse pole figure (IPF) images of an Alloy 600 diffusion bonded joint and an Alloy 182 fusion-weld, respectively. For the diffusion-bond joint (Fig. 1a), the presence of a diffusion bond line can clearly be seen between the two different matrices. It should be noted that, despite the PBHT, grain growth across the bond-line was not observed, probably due to the relatively low PBHT temperature. Meanwhile, the fusion weld (Fig. 1b) shows a typical elongated grain structure as observed previously [20].

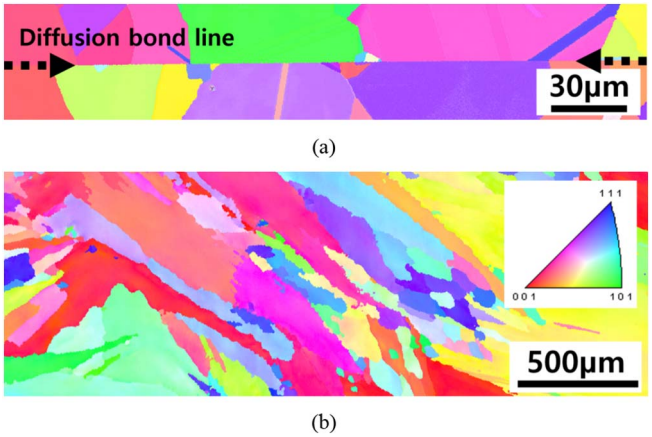

Fig. 1. Surface EBSD inverse pole figure images of (a) Alloy 600 diffusion bond region and (b) Alloy 182 fusion-weld.

2.2. High-temperature S-CO_2 Corrosion Test

A detailed description for the high-temperature S-CO_2 corrosion test set-up can be found in a previous paper by the authors [6]. Once the corrosion coupons and mini-tensile specimens were loaded in the autoclave, the system was purged with research-grade CO_2 gas (99.999% purity with less than 1 ppm of O_2 and H_2O) several times to remove the impurity. During the corrosion test, liquid CO_2 was fed to the system by a high pressure CO_2 pump at a constant flowrate of 5 mL/min. Then, liquid CO_2 was pre-heated to 400 °C and became a supercritical fluid while passing through a helical-type tube in a preheater. The S-CO_2 was fed into the autoclave and fully heated to the target test temperatures (550 and 650 °C). During the test period of 1000 h, pressure was maintained at 20 MPa. At least 2 coupon specimens were used at each condition.

After the corrosion tests, the weight gains of coupon specimens were measured using a microbalance with a resolution of 0.001 mg (Mettler Toledo AT21 Comparator), and then, one of the samples was used for oxide characterization by an X-ray diffractometer (XRD, RIGAKU D/MAX-2500). For diffusion-bonded specimens, the weight measurements were not performed since other than the presence of narrow diffusion bond line, they were mostly Alloy 600 base materials. Therefore, the weight gain results of diffusion-bonded samples would be the same as that of Alloy 600 base materials, which was already reported by the authors [6]. Meanwhile, the following analyses were conducted for both diffusion-bonded joints and fusion-welds. Oxide surface morphology and cross-sectional microstructure observation were performed by focused ion beam (FIB, Helios Nanolab 450 F1) equipped with scanning electron microscope (SEM). For the detailed characterization of the oxide structure and underlying matrix, a transmission electron microscope (TEM, Titan cubed G2 60-300) equipped with energy-dispersive spectroscope (EDS) was used for the samples prepared by FIB. In addition, a secondary-ion mass spectrometer (SIMS, CAMECA IMS 7f), TEM/EDS and electron energy-loss spectroscopy (EELS) were used to analyze for the presence and distribution of C in the oxide layer and the underlying matrix. Tensile testing of fusion-welds was performed before and after S-CO_2 exposure. The tensile test results of diffusion-bonded specimens were not included since those were already reported by the authors [19]. Briefly, it showed that the changes of tensile properties were not significant after exposure to S-CO_2 at 550 and 600 °C up to 3000 h. A test matrix including type and number of specimens used in this study is listed in Table 2.

3. Results and Discussion

3.1. Corrosion and Carburization Behavior of Alloy 600 Diffusion-bonded Joint

The near-surface cross-section of the diffusion-bonded specimen exposed to S-CO_2 at 650 °C (20 MPa) for 1000 h was observed by FIB and the results are shown in Fig. 2. The FIB cross-sectioning had to be carried out several times to locate the diffusion bond line, as it could not be distinguished from the plan-view of the oxidized surface. The oxide morphology over the bond line was the same as that on adjacent Alloy 600 base metal. Fig. 2a is a cross-sectional SEM micrograph showing a thin and continuous oxide layer (dark grey line between Pt coating and matrix) on the surface, underlying fine-grained region, and