Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 12-13, 2016

Surface and Grain Boundary Oxidation of Ni-Based Alloys in Hydrogenated Water

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1. Introduction

Primary water stress corrosion cracking (PWSCC) of Ni-based Alloy 600 (Ni-16Cr-8Fe in wt%) has been a challenge in terms of material failure on the primary side of pressurized water reactors (PWRs) [1]. Given that PWSCC is linked to intergranular stress corrosion cracking (IGSCC) in most cases, it appears that understanding the corrosion behavior of grain boundaries is crucial with regard to PWSCC. The intergranular oxidation of Alloy 600 by exposure to primary water is known to be detrimental to grain boundary cohesion [2,3]. Changes in the grain boundary structure and chemistry due to oxygen penetration can increase the sensitivity to PWSCC under a load, because intergranular oxidization significantly weakens the strength of the grain boundary itself [2] or the interface between the oxidized grain boundary and the matrix [3].

The aim of the present study was to analyze the intergranular oxidation phenomenon systematically and thereby obtain clear insight into intergranular cracking in Alloy 600 when it is exposed to primary water, thus simulating the normal operating conditions of a PWR. Because the grain boundary characteristics can significantly affect the degree of intergranular oxidation, their roles with regard to intergranular oxidation susceptibility were also investigated. Finally, the possible correlations between intergranular oxidation and intergranular cracking in this alloy are discussed based on the observed results.

2. Methods and Results

2.1 Specimen Preparation

The test specimens were taken from a round mill-annealed Alloy 600 bar with an outer diameter of 120 mm. The material was finally heat-treated at 950 ℃ for 3 hours, and the chemical composition (wt%) was measured to be 75.8 Ni, 15.45 Cr, 6.98 Fe, 0.055 C, 0.48 Si, 0.60 Mn, 0.18 Ti, 0.06 Co, 0.17 Al, 0.03 Cu, 0.005 P, and 0.001 S. The material used in the present study was the same as that manufactured for CRDM nozzles in some domestic nuclear power plants. From a preliminary examination of the bar, it was proved that the microstructure is homogeneous and isotropic, irrespective of its location and orientation.

80 mm wide x 40 mm deep x 1.5 mm thick specimens were taken from the round bar for an immersion test. Since the properties of the oxide layer and grain boundary oxidation are considerably sensitive to the surface state of a specimen under test, all specimens were finally polished down using 0.3 ㎛ alumina powders in the same way before immersion in the autoclave. This was done both to minimize the surface damage layers formed by grinding, and to give all the specimens the same surface state.

2.2 Immersion Test and Microscopic Examination

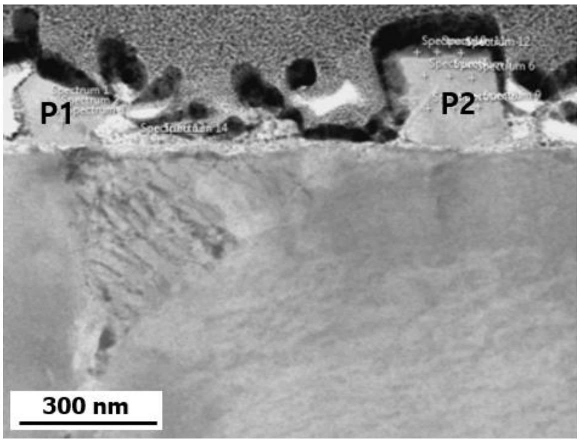
An immersion test was conducted for 5 months in a simulated PWR primary water environmental condition, that is, 1200 ppm B (weight) as H_3BO_3 and 2 ppm Li (weight) as LiOH in pure water, at a temperature of 325 ℃, dissolved oxygen content below 5 ppb, a hydrogen content of 30 cc/kg H_2O, and an internal pressure of 2300 psi.

After the immersion test, the specimens were investigated using microscopic equipment, such as optical microscopy, SEM, and TEM. The specimens for the optical microscopy and SEM were prepared by chemical etching in a solution of 2 % bromine + 98 % methanol. The TEM foils containing surface oxide layers and grain boundaries were prepared through FIB milling using a dual beam Hitachi FIB-2100 system with a Ga^+ incident beam energy of 30 kV and a current of 1 – 5 nA. To eliminate the deformed surface layers generated from the sputtering of high energy Ga ions, subsequent ion milling was conducted with Ar ions with an incident beam energy of 300 V at an incidence angle of 10°for 10 minutes.

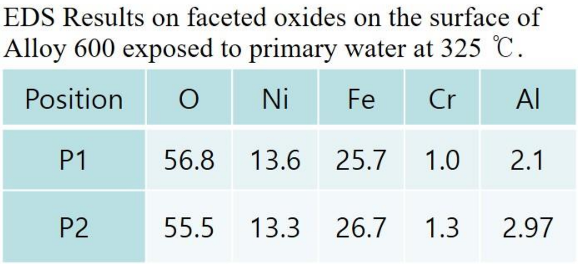
An SEM examination was performed using a JEOL 5200 (operating voltage 25 kV) and a JEOL 6300 (operating voltage 20 kV). A TEM analysis was carried out with a JEOL JEM-2100F (operating voltage 200 kV) equipped with an Oxford ISIS EDS system.

2.3 Surface Oxidation of Alloy 600

Fig. 1(a) shows a STEM image in which the locations for the EDS point analyses of the faceted oxides on the surface are shown (denoted as P1 and P2). The structure of the oxides was identified as FCC with a lattice constant of 0.834 nm. The chemical compositions of the faceted surface oxides P1 and P2 are provided in Fig. 1(b). The stoichiometric ratios of O:Ni:Fe were approximately 4:1:2. Therefore, it can be concluded that the oxide is $NiFe_2O_4$ with minor cations of Cr and Al. Similar results were reported by others for Alloy 600 [4], and for Alloy 690 [5] in simulated PWR primary water environments. The main source of Fe ions likely originated from the stainless steel autoclave itself and/or the internal structural components inside the autoclave [4].



(a)



EDS Results on faceted oxides on the surface of Alloy 600 exposed to primary water at 325 ℃.

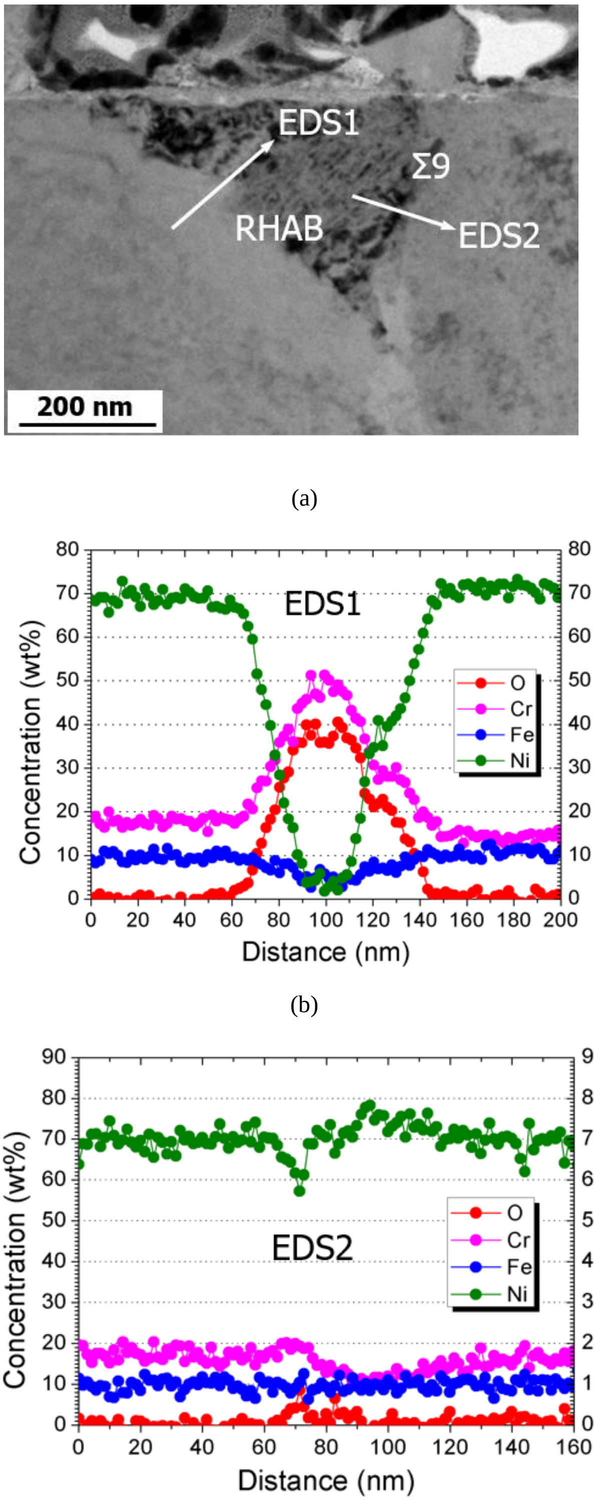
Position	O	Ni	Fe	Cr	Al
P1	56.8	13.6	25.7	1.0	2.1
P2	55.5	13.3	26.7	1.3	2.97

(b)

Fig. 1. (a) STEM image around a surface and (b) chemical compositions of the surface oxides.

2.4 Intergranular Oxidation of Alloy 600

The results of the EDS line profiles across the grain boundaries on the surface are given in Fig.2. The locations and directions of the measurement are denoted by the arrows in Fig. 2(a). From the line profiles 'EDS1' of the left grain boundary shown in Fig. 2(b), oxygen and Cr were strongly detected, whereas Fe and Ni were severely depleted inside the grain boundary. This indicates that Cr oxide precipitated inside the grain boundary and that Fe and Ni diffused into the outer environment. On the other hand, the right grain boundary shown in Fig. 2(c) was also oxidized, because oxygen was detected on that grain boundary. However, the degree of intergranular oxidation was insignificant compared to that of the left grain boundary.



(a)

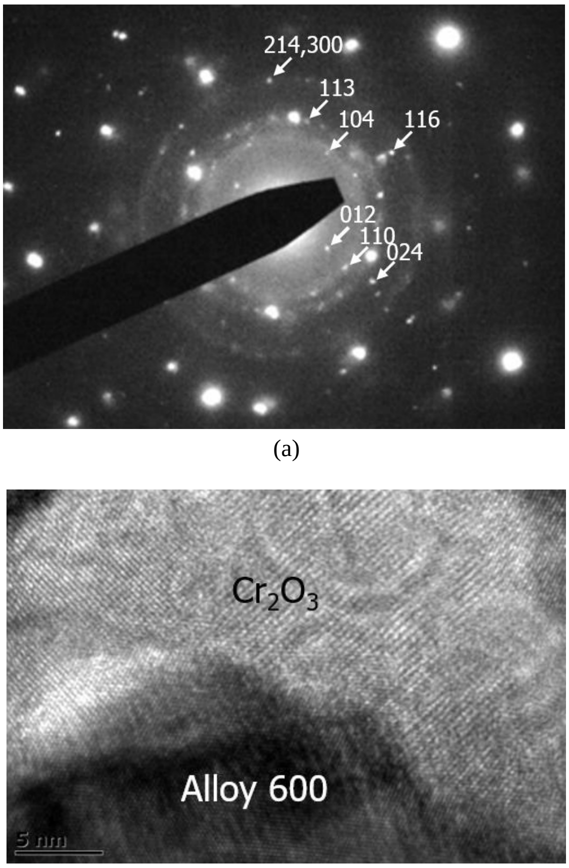
(b)

(c)

Fig. 2. (a) TEM image of the oxidized grain boundaries, compositional profiles of O, Cr, Fe and Ni across the (b) left, and (c) right grain boundary.

2.5 Crystallographic Investigation

Crystallographic investigations were done to identify the crystal structure of the grain boundary oxides and their orientation relationships with the matrix. Fig. 3(a) shows a selected area diffraction pattern taken from the oxidized region. It was clearly identified that the spots and rings from the oxidized region originated from Cr_2O_3. Cr oxides in the crack tips, the surface oxide layers, and oxidized grain boundaries are consistently found to be Cr_2O_3 in Ni-based alloys. Fig. 3(b) shows a HRTEM lattice image of the oxidized zone. Form this figure, it can be identified that nano-crystalline Cr_2O_3 oxides 10 nanometers or less in size were randomly distributed inside the oxidized zone. Specific orientation relationships of Cr_2O_3 with the Alloy 600 matrix or the Ni-rich zone were not found. Sennour et al. [6] also revealed that Cr_2O_3 did not show an orientation relationship with respect to the matrix.



(a)

(b)

Fig. 3. (a) Selected area diffraction pattern, and (b) HRTEM image from an oxidized grain boundary

3. Conclusions

In the present study, the surface oxide layer and grain boundary of Alloy 600 tested at 325 ℃ in a simulated primary side environment of a PWR were analyzed through XRD, SEM and TEM/EDS. Most of the important experimental results obtained are believed to correlate with the oxidation penetration into the material. Intergranular oxidation of Alloy 600 was revealed to be a common phenomenon in PWR primary water, and it was clearly shown that intergranular oxidation by pre-exposure to primary water caused embrittlement of the grain boundaries. It was also revealed that the degree of intergranular oxidation due to oxygen diffusion at each grain boundary reflected the IGSCC behavior of the cracked Alloy 600 specimens well. Intergranular oxidation is scarcely found in Alloy 690, which is more resistant to PWSCC, and in which cracks are known not necessarily to propagate along the grain boundaries [7,8]. Therefore, all of these considerations strongly suggest that intergranular oxidation, which induces the formation of Cr oxide and its resultant alteration of the grain boundary structure and chemistry in Alloy 600, can be regarded as phenomenon preceding intergranular cracking in PWR primary water.

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