

Influence of Surface Conditions on Primary Water Stress Corrosion Cracking of Alloy 600

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1. Introduction

Ni-based alloy 600, which has been used widely for structural components in nuclear power plants, is known to be highly susceptible to primary water stress corrosion crack (PWSCC) in the primary water environments of a pressurized water reactor (PWR) [1]. Laboratory testing and service experiences have clearly shown that the predominant failure mode of alloy 600 in PWR primary water is nearly always intergranular (IG) SCC (IGSCC), which means that grain boundaries are the preferential paths for cracking. Many factors causing PWSCC initiation of alloy 600 are existed, and the surface oxidation behavior was reported to affect the crack initiation of this alloy [2]. The surface finish is an important factor influencing the oxidation behavior of an alloy. According to Perez et al. [3], the surface finish produces a subsurface deformation layer with a high dislocation density, phase transformation and recrystallization, which would influence on affect oxidation behavior. Therefore, the influence of surface conditions on PWSCC of alloy 600 needs to be understood. The objective of the present study is to analyze the surface and intergranular oxidation behavior depending on the surface condition of alloy 600, and to reveal the effects of the oxidation behavior on PWSCC. Immersion tests were conducted in a simulated PWR primary water environment at 325 °C for 10, 100 and 1000 hours. The oxidized specimens were precisely characterized using an optical microscope, scanning electron microscope (SEM), transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectroscopy (EDS).

2. Methods and Results

2.1 Materials and Specimen Preparation

The material used in this study was taken from round bars of mill-annealed alloy 600. Its composition is shown in Table 1. Specimens with dimensions of 8×8×1 mm³ were prepared from the alloy for an immersion test. The specimens were categorized as grinding, polishing and chemical polishing. Grinding was mechanically ground with waterproof abrasive paper up to 400 grit, polishing was mechanically ground to 2000 grit and then polished using 0.3 μm alumina powders. And

chemical polishing was conducted in a 2 % bromine + 98 % methanol solution for 15 sec after polishing.

2.2 Immersion Test and Microscopic Examination

The specimens used to observe the microstructures of alloy 600 samples were prepared by chemical etching in a solution of 2 % bromine + 98 % methanol. The immersion test was conducted for 10, 100 and 1000 hours under simulated PWR primary water conditions, i.e., 1200 ppm B (weight) and 2 ppm Li (weight) in pure water at 325 °C with a dissolved oxygen content of less than 5 ppb and a hydrogen content of 30 cm³/kg H₂O. After the immersion test, the oxidized specimens were investigated using an optical microscope, SEM, TEM, and an EDS. The SEM examination was conducted using an FEI Sirion (operating voltage 10 kV). A TEM samples containing the surface oxidation layer and grain boundaries were prepared with focused ion beam (FIB) milling using a dual-beam Scios 2 system with Ga+ incident beam energy of 30kV and a current of 77 pA - 7 nA. STEM/EDS analysis was carried out with a JEOL JEM-2100F (operating voltage 200 kV) equipped with an Oxford Instruments X-Max 80T Silicon Drift Detector and an AZTEC analysis system (Ver. 3.1b). There is intrinsic overlap between the peaks of the oxygen K line and the Cr L_α line. Therefore, deconvolution of the overlapping spectral peaks was carried out for a clear elimination of artifacts possibly originating from the overlapping of the peaks.

Table I: Chemical compositions of alloy 600 (wt%)

	Ni	Cr	Fe	C	Si	Ti	Al	P	S
Alloy 600	75.80	15.45	6.98	0.055	0.48	0.18	0.171	0.005	0.001

2.3 Surface oxide morphology

Fig. 1 shows the surface oxide morphologies depending on the surface conditions of alloy 600 samples tested for 1000 hours. As shown in the figures, the oxidized samples were covered with polyhedral crystals and filamentous shaped oxides on the entire surface areas irrespective of the treatment. Also, the grain boundaries can be observed in chemically polished sample (Figs. 1(c)) due to the etching effects, but not in the ground and polished samples (Figs. 1(a) and (b)).

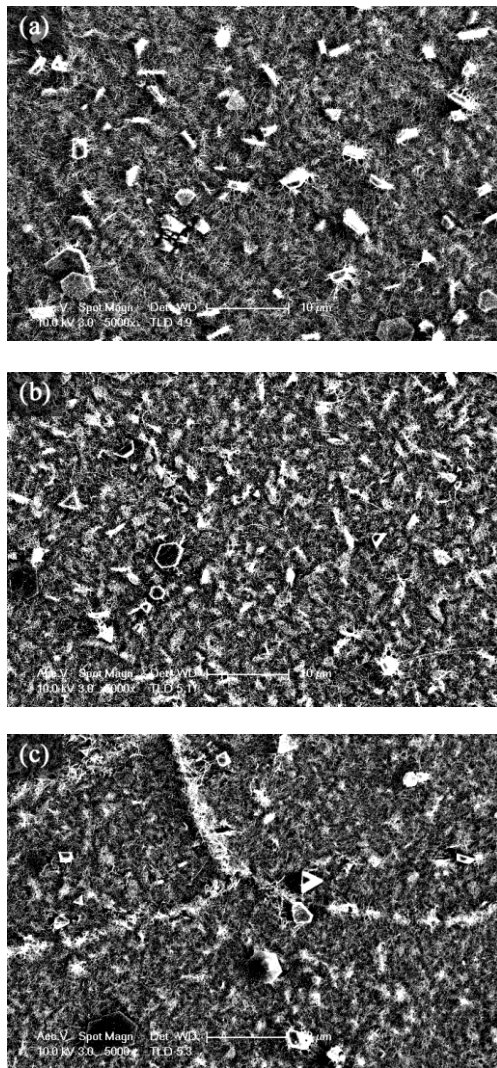


Fig. 1 Surface oxide morphology of alloy 600 samples after immersion 1000 hours with different surface conditions (a) grinding, (b) polishing and (c) chemical polishing.

2.4 FIB TEM sample preparation procedures

To investigate oxidation phenomena on grain boundaries, FIB was adopted to prepare TEM samples in this study. Fig. 2 shows the TEM sample preparation procedure for a polished sample which cannot observe grain boundaries on the surface. First, as shown in Fig. 2(a), the surface was ion-milled to $20 \times 12 \mu\text{m}$ size to find the grain boundaries, drawn the imaginary extension line connecting the found grain boundary. And then, platinum was deposited on the middle of the predicted grain boundary to prevent damage. Fig. 2(b) shows two trenches ion-milled in front and behind of deposited platinum strip. To lift-out, the sample and a probe were deposited with platinum. Fig. 2(c) shows the sample attached to a TEM grid with Pt deposition. The specimen was thinned using a beam with 30 kV and 5

nA. Finally, a beam with 5 kV and 77 pA was used to minimize the deformed surface layers.

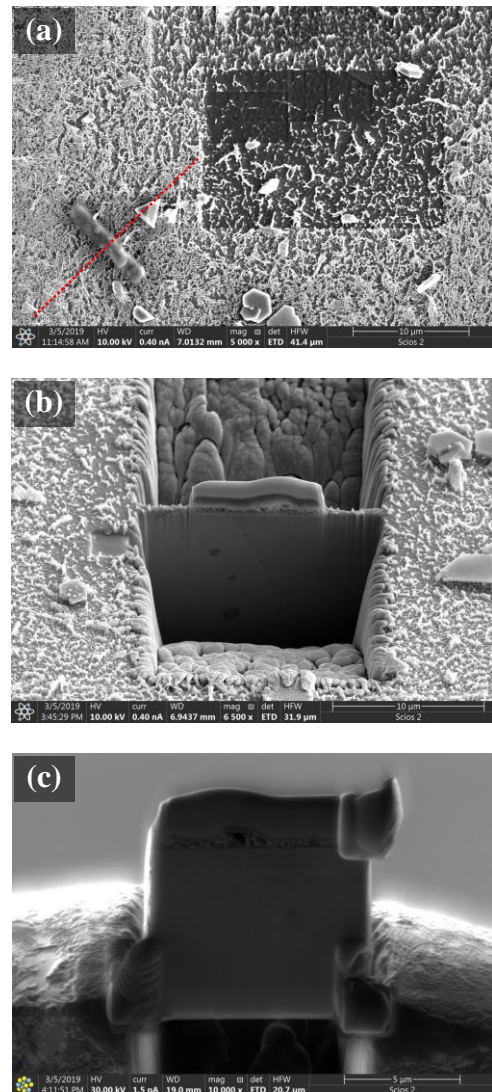


Fig. 2 Images showing several steps during FIB-based TEM sample preparation. (a) the image after milling the surface oxides (b) the image showing the 2 trenches ion-milled in front and behind platinum strip deposited on the surface (c) the image of the sample attached to a TEM grid.

2.5 STEM/EDS analysis

Fig. 3(a) shows a STEM image of a ground sample, and Figs. 3(b)-(e) are compositional maps of Cr, Fe, Ni and O. It was observed that the oxides were formed on the surface and the internal oxide layer was formed inside the surface. The most important feature found in this figure is that oxygen was not detected along a grain boundary in the ground sample. Fig. 4 shows a STEM image and composition maps of a chemically polished sample. The internal oxide layer of the chemically polished sample appears to be thinner than that of the ground sample. Also the interesting feature in the figure

is that oxygen was detected along the grain boundary, contrary to the case of the ground sample. This means that oxygen diffused into the grain boundaries. The alterations of the grain boundary structure and chemistry owing to oxygen penetration can increase the sensitivity to PWSCC since grain boundary oxidation significantly weakens the grain boundary strength, as reported by Fujii et al [4]. Scenini et al. [5] showed from a systematic study on the crack initiation of alloy 600 that electro-polished samples were more prone to PWSCC than mechanically polished ones. Therefore, it is believed that chemical polishing causes grain boundary oxidation and increases the sensitivity to PWSCC.

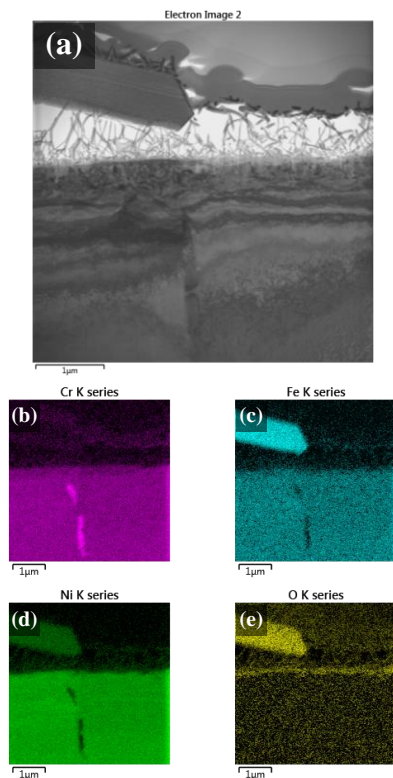


Fig. 3 (a) STEM image and composition maps of (b) Cr, (c) Fe, (d) Ni, and (e) O around the surface of a ground alloy 600 sample.

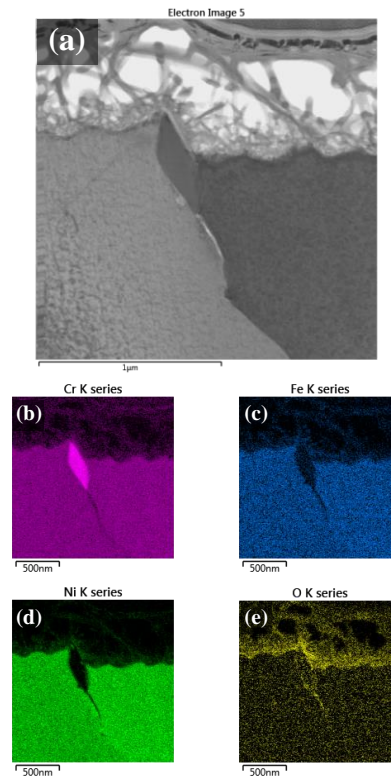


Fig. 4 (a) STEM image and composition maps of (b) Cr, (c) Fe, (d) Ni, and (e) O around the surface of a chemically polished alloy 600 sample.

4. Conclusion

In the present study, surface oxides and internal oxide layers on the differently surface-treated alloy 600 samples tested at 325 °C in a simulated primary water environment were analyzed with optical microscope, SEM and STEM/EDS. The main objective of study was to observe the oxidation behavior depending on the surface condition, and to reveal the effects of surface oxidation on PWSCC. As a result, the oxygen penetration along the grain boundaries was observed only in the chemically polished sample. Therefore, it is considered that the smaller the surface deformation, the easier the grain boundary diffusion of oxygen and it causes IGSCC of alloy 600 more easily in primary water environments of a PWR.

REFERENCES

- [1] W. Bamford and J. Hall, A Review of Alloy 600 Cracking in Operating Nuclear Plants: Historical Experience and Future Trends, 11th Int. Conf. on Environmental Degradation of Materials in Nuclear Systems, Stevenson, WA, Aug. 10-14, 2003, pp. 1071-1081
- [2] J. Panter, B. Viguier, J.-M. Cloué, M. Foucault, P. Combrade and E. Andrieu, Influence of oxide films on

primary water stress corrosion cracking initiation of Alloy 600, *J. Nucl. Mater.* 348 (2006) 213–221.

[3] S.L Perez, D.W. Saxey, T. Yamada and T. Terachi, Atom-probe tomography characterization of the oxidation of stainless steel, *Scripta Mater.* 62 (2010) 855-858

[4] K. Fujii, T. Miura, H. Nishioka and K. Fukuya, Degradation of grain boundary strength by oxidation in alloy 600, *Proceedings of the 15th Int'l Conf. on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactor*, TMS, 2011, pp. 1447-1458.

[5] F. Scenini, R. C. Newman, R. A. Cottis, R. J. Jacko, Effect of Surface Preparation on Intergranular Stress Corrosion Cracking of Alloy 600 in Hydrogenated Steam, *CORROSION*. 2008;64(11):824-835.