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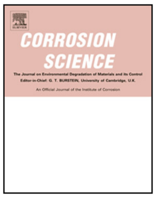

Effect of electropolishing on corrosion of Alloy 600 in high temperature water

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ABSTRACT

Effect of change in surface composition and microstructure by electropolishing on corrosion of Alloy 600 in high temperature water was investigated. The investigation was conducted by comparing the corrosion of electropolished surface (EPS) with that of the 40 nm-colloidal silica slurry polished surface (CPS), which has few composition change as well as few surface residual strain. The result revealed while EPS had a thicker oxide scale at the early stage of corrosion, it showed a lower corrosion rate when the exposure time was >25 h. This is attributed to formation of a Cr-enriched oxide film at the primary surface by electropolishing.

1. Introduction

Stress corrosion cracking (SCC) of structural materials is one major concern in light water reactors, which is a synergic effect of material, mechanics, and environment [1–4]. According to internal oxidation and slip-dissolution/oxidation mechanisms, surface corrosion behaviour plays an important role in SCC initiation process [5–12]. Surface state following various grinding and polishing processes is a key factor influencing the corrosion behaviour [10,11]. To date, a number of studies have been carried out to clarify the effect of surface state on corrosion of austenitic stainless steels and nickel-base alloys in high temperature water, which showed that the ground, mechanical polished and electropolished surfaces had different corrosion behaviours [13–25]. The effect of electropolishing on corrosion is one focus of these studies. In deaerated high temperature water, Ziemniak found that the electropolished surface (EPS) of 304 stainless steel had a lower corrosion rate than mechanical polished surface [23]. However, other researchers concluded oppositely [21,24]. Despite the discrepancy in these studies, discussions on the role of electropolishing had been focused on the effect of removal of surface residual strain by electropolishing. The effect of change in surface chemical composition following electropolishing, on the other hand, has not been considered. Due to dissolution of the metallic elements during electropolishing, composition of the surface after electropolishing very likely differs to that of the bulk alloy and is expected to vary the corrosion behaviour.

The 40 nm-colloidal silica slurry is usually used for the final process of mechanical polishing. Polishing using the slurry could remove the surface residual strain but lead to few composition change at the surface. As such, comparison of the corrosion behaviour following electropolishing and the slurry polishing could clarify the effect of surface composition change by electropolishing on corrosion. In this study, corrosion behaviour of Alloy 600 in deaerated high temperature water was studied by exposure tests following electropolishing and the colloidal silica slurry polishing, in an effort to improve the understanding of the surface composition change by electropolishing on corrosion. Corrosion behaviour following the exposure tests were analyzed by using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and transmission electron microscope (TEM).

2. Experimental

The material used for the experiment was mill-annealed Alloy 600, with a chemical composition listed in Table 1. Corrosion coupons of 10 mm × 10 mm × 1 mm cut from the alloy were ground using SiC papers up to 2000 grit, and then polished by diamond pastes of 1.5 μm and 0.5 μm. At the final step, the coupons were polished by electropolishing and 40-nm colloidal silica slurry, respectively. The electropolishing was conducted in an electrolyte at 70 °C for 30 s at 0.2 A. The electrolyte was prepared by 15 vol% sulfuric acid of 98 wt% concentration, 64 vol% phosphoric acid

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Table 1
Chemical composition (wt%) of Alloy 600.

C	Mn	Fe	S	Si	Cu	Cr	P	Nb	Ti	Ni
0.065	0.22	9.50	0.0021	0.12	0.1	15.57	0.007	<0.05	0.28	Bal.

of 85 wt% concentration and 21 vol% water. The slurry polishing employed a period of >2 h to ensure the removal of surface residual strain. Following the electropolishing and the slurry polishing, all the coupons were ultrasonically cleaned in pure water and ethanol–acetone mixture, and then were dried in air.

A low flow rate (~100 mL/min) refreshed loop equipped with a 3-L autoclave made of 316 stainless steel was used for the exposure tests in simulated primary water at 320 °C. The water contains 1000 ppm (defined by mass, the same hereafter) B^{3+} as H_3BO_3 and 2 ppm Li^+ as LiOH. Dissolved oxygen (DO) in the inlet water was controlled at <5 ppb (defined by mass, the same hereafter) by bubbling pure N_2 gas in the water tank. Before ramping the autoclave to high temperature, the water tank was N_2 gas bubbled to deoxygenate the inlet water to <5 ppb DO. Then the autoclave was heated up to 50 °C and kept for 1 day while the N_2 gas bubbling of the water tank was continuing. This process was employed to remove oxygen in the loop with a high efficiency. To study the corrosion kinetics, in total five exposure periods at 1, 5, 25, 120 and 500 h were employed for the tests.

Following the exposure tests, characterization of the oxide scale formed on the colloidal silica slurry polished surface (CPS) and EPS was conducted to clarify the corrosion behaviour. A FEI XL30 Field Emission Gun Scanning Electron Microscope (FEG-SEM) was used for observation of the surface morphology of the oxide scale. An ESCALAB 250 X-ray Photoelectron Spectroscopy was used to characterize the depth profile of the oxide scale. The XPS analysis was conducted by sequential sputtering of the oxides using a 2 keV Ar ion beam rastering an area of 2-mm diameter. The sputtering rate was determined to be 0.1 nm/s with reference to Ta_2O_5 layer. According to Ref. [12], there is only small difference in sputtering rates of typical oxide spinels of Fe_3O_4 (0.157 mol cm^{-3}) and $FeCr_2O_4$ (0.155 mol cm^{-3}). The XPS spectra were obtained over a 0.5-mm spot using a focusing X-ray monochromator. Chemical states of Cr, Ni and Fe at the primary surface after polishing were analyzed by normalizing values of each element peak area by multiplying sensitivity factors [12]. Before peak fitting, the possible eigen values were determined by analyzing all data. In the case of Cr, for example, three eigen spectra were identified to be corresponding to Cr(0), $Cr(OH)_3$ and Cr(III) in oxides. Then analysis of the data was performed via XPSpeak4.1 peak fitting software. The C1s peak from adventitious carbon at 285 eV was used as a reference to correct the charging shifts. Some flexibility is permitted in the XPSpeak4.1 software to determine the existence of peak values and the area of each element value. Cross-sections of the oxide scale formed on CPS and EPS following the 500-h exposure were selected for the observation and analysis by a FEI TECNAI G2 F20 Transmission Electron Microscope. Composition profiles were analyzed by energy dispersive X-ray spectroscopy (EDX) using point- and area scans. Since the TEM used is incapable of convergent-beam electron diffraction, only large oxide particles with the size of >100 nm was selected for electron-diffraction analysis. The TEM samples were prepared by a FEI QUANTA 200 3D focus ion beam (FIB) system.

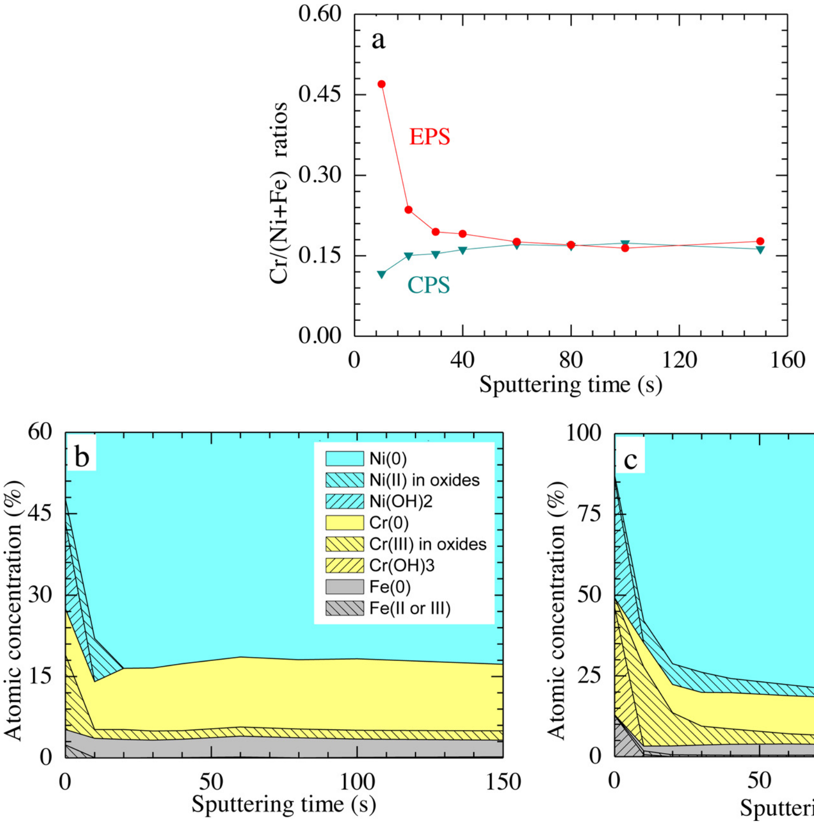

Fig. 1. Characterization of the primary surface state by XPS following colloidal silica slurry polishing and electropolishing. (a) Depth profile of the atomic ratio of Cr/(Ni + Fe) analyzed on CPS and EPS, and speciated composition depth profiles of Cr, Ni and Fe analyzed on CPS (b) and EPS (c).

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