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Characterization of interfacial reactions and oxide films on 316L stainless steel in various simulated PWR primary water environments

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HIGHLIGHTS

- Long-term EIS measurements of 316L SS in simulated PWR primary water.
- Highest charge-transfer resistance and oxide film resistance in oxygenated water.
- Highest electric double-layer capacitance and oxide film CPE in hydrogenated water.
- Similar compositions, different shapes of oxides in deaerated/hydrogenated water.
- Inner layer Cr-rich in hydrogenated/deaerated water, Ni-rich in oxygenated water.

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ABSTRACT

The effect of water chemistry on the electrochemical and oxidizing behaviors of 316L SS was investigated in hydrogenated, deaerated and oxygenated PWR primary water at 310 °C. Water chemistry significantly influenced the electrochemical impedance spectroscopy parameters. The highest charge-transfer resistance and oxide-film resistance occurred in oxygenated water. The highest electric double-layer capacitance and constant phase element of the oxide film were in hydrogenated water. The oxide films formed in deaerated and hydrogenated environments were similar in composition but different in morphology. An oxide film with spinel outer particles and a compact and Cr-rich inner layer was formed in both hydrogenated and deaerated water. Larger and more loosely distributed outer oxide particles were formed in deaerated water. In oxygenated water, an oxide film with hematite outer particles and a porous and Ni-rich inner layer was formed. The reaction kinetics parameters obtained by electrochemical impedance spectroscopy measurements and oxidation film properties relating to the steady or quasi-steady state conditions in the time-period of measurements could provide fundamental information for understanding stress corrosion cracking processes and controlling parameters.

1. Introduction

Austenitic stainless steels (SS) are widely used in pressurized water reactor (PWR) nuclear power plants as important structural materials due to their combined good mechanical properties and corrosion resistance. The corrosion resistance due to the passive film formed on the surfaces of austenitic alloys in high-temperature water environments during the reactor operation is of great importance. The nucleation and propagation of localized corrosion, and stress corrosion cracking (SCC) in particular, are generally recognized to be related to the properties of the oxide film formed on the metal surface [1–8]. Water chemistry exerts a significant influence on the oxide film properties and is related to the oxidation kinetics [9–15]. The hydrogenated water chemistry in the PWR water has been applied to maintain a relatively low electrochemical corrosion potential to reduce the SCC susceptibility of the materials [10] The normal range of the dissolved hydrogen (DH)

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concentration in operating PWR plants is 25–50 cm^3 (STP) H_2/kg H_2O [16]. Oxygen could be introduced into the primary loop system by adding aerated water, or by adding oxygen or H_2O_2 during the plant shutdown process for PWRs. This would stabilize the oxide and thus decrease the release of radioactive species into the coolant [10].

It has been reported that the duplex oxide film formed on stainless steels in high-temperature water contains more Cr in the inner layer and more Fe in the outer layer. Several different mechanisms of high-temperature aqueous oxidization were proposed to rationalize this phenomenon [17–19]. Stellwag [17] suggested that the formation of the inner layer could be related to a solid-state growth mechanism. The formation of the outer, coarse-grained oxide layer was because of the precipitation of dissolved metal ions. The enrichment of chromium in the inner layer could be explained by preferential dissolution of Fe and Ni during passivation and to the low diffusivity and solubility of chromium in the spinel lattice. Ziemniak et al. [18] thought that corrosion occurred in a non-selective manner and that the formation of the corrosion film consisted of two spinel oxide layers with similar compositions implied that immiscibility played an important role in the phase separation process. Robertson [19] found that the corrosion rate of SS in high temperature was controlled by the solid-state diffusion of Fe ions along grain boundaries in the oxide layer. A duplex layered oxide was formed with the inner layer growing by the ingress of water along oxide micropores and the outer layer growing by the diffusion of metal ions. The location of an alloy component across the oxide layer depended on its diffusion rate in the oxide.

The oxide films formed on austenitic SS in high-temperature water environments are closely related to water chemistry [10–15]. Kim [11] found that the oxide film formed on SS in cyclic normal and hydrogen water chemistries mainly consisted of two layers: an outer layer with large spinel particles and small hematite particles and a fine-grained inner layer of chromium-enriched spinel. Kumai and Devine [12] suggested that the outer oxide layer formed on 304 SS was composed of M_3O_4 when dissolved oxygen (DO) was below a critical value; as DO increased, M_2O_3 particles gradually formed with roughening of the preformed M_3O_4 particles. Kuang [13] investigated the characteristics of the oxide films formed on 304 stainless steel at different DO concentrations in 290 °C water. Less hematite and more spinel oxides formed on a fresh sample as the DO decreased. Meanwhile, the relative Cr content in the film increased. Terachi et al. [20] found that the corrosion rate of 316L SS increased slightly with increasing DH concentration in simulated PWR primary water. Han et al. [21,22] found that the oxide film of 316L SS formed in hydrogenated and deaerated PWR water was Cr-rich in the inner layer and Fe-rich in the outer layer. Xu et al. [10] reported that in cyclic hydrogenated and oxygenated water chemistry in high temperature water, the film resistance during the periods of DO was much higher than that during the periods of DH for 316 SS.

The SCC behaviors of austenitic alloys in high-temperature water are also affected by water chemistry. It was found that for the 316L HAZ in a boiling water reactor (BWR) environment, switching the water chemistry from oxygen-bearing water to hydrogen-bearing water drastically decreased the electrochemical potential and the crack growth rate [23]. It was reported that on cold-rolled 316L, more extensive intergranular stress corrosion cracks were found in deaerated PWR water than in hydrogenated PWR water [24]. The crack growth rate (CGR) decreased with the changing water chemistry from 2 ppm DO in oxygenated water to de-oxygenated water with DO < 5 ppb, and decreased further after changing to hydrogen-saturated water for 3D cold-rolled 316NG SS in BWR water [25]. Andresen et al. [26] found that there was a peak in crack growth rate vs. dissolved hydrogen in BWR water. In a PWR environment, it was found that the CGRs of 316L HAZ increased with increasing DO, and CGR in hydrogenated water was approximately one order of magnitude slower than in oxygenated water [27]. Meng et al. [28] found that the CGRs of cold-rolled 316L SS in simulated PWR water were not affected by the DH when it was lower than 5 cm^3 (STP) H_2/kg H_2O and that the SCC growth rate decreases with increasing DH in the range of 5–50 cm^3 (STP) H_2/kg H_2O. It was also found that the corrosion potential of stainless steel was weakly dependent on the DH, while the crack growth rate showed a significant decrease with increasing DH [28].

The possibility of predicting SCC from electrochemical measurements has aroused considerable interest in the nuclear industry [29]. Electrochemical monitoring can obtain in-situ information on water chemistry and corrosion conditions relevant for light water reactor systems. The applications of electrochemical monitoring in nuclear power environments include: optimization of hydrogen addition during hydrogen water chemistry in BWRs, hydrogen control in the primary system of PWRs and oxygen control and detection of redox transients in PWR secondary systems [30]. Electrochemical corrosion potential (ECP) monitoring is an important factor in operating BWR environments [31]. Reduction of ECP of the BWR vessel and internal stainless steel surfaces is essential for mitigating intergranular stress corrosion cracking (IGSCC) [32]. Andresen et al. [5] reported that the CGRs of cool worked 300 series SS in high-temperature pure water containing 2000 ppb DO decreased with a decreasing corrosion potential. In PWR environments, measuring ECP is an effective way to assess irradiation-assisted stress corrosion cracking (IASCC) which is influenced by high-temperature water environment, mechanical stresses and the presence of irradiation. It determines whether it is likely that IASCC occurs (a high value of the potential) or not (a low value) [33]. Arioka et al. [6] found that the IGSCC growth rate of non-sensitized, cold-worked 316 SS in a simulated PWR environment decreases gradually with a decrease in the electrochemical potential. It is necessary to clarify the relationship between electrochemical behavior and oxide film properties of SS in high-temperature high-pressure aqueous environments for a mechanistic understanding of the corrosion and SCC behaviors of SS in nuclear plant coolant environments.

The objective of this work is to investigate the effects of various water chemistries on the electrochemical behavior and oxide film properties of 316L SS in simulated PWR primary water environments including hydrogenated, de-aerated and oxygenated water. Long-term electrochemical impedance spectroscopy (EIS) measurements of the interfacial kinetics are used in combination with the characterization of oxide films by Raman spectral analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observation.

2. Experimental

The elemental composition of the 316L SS used in the present work is listed in Table 1.

Samples were cut from a 22-mm-thick plate. The plate was solution-annealed (SA) at 1100 °C for 2 h followed by a water quench. The size of the specimen for exposure and electrochemical test was 10 mm × 10 mm × 3 mm. They were mechanically abraded

Table 1
Chemical composition (wt.%) of 316L SS.

C	Si	Mn	S	P	Cr	Ni	Mo	Fe
0.019	0.320	1.60	0.006	0.027	16.39	10.21	2.12	Bal.