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The effects of temperature and aeration on the corrosion of A508III low alloy steel in boric acid solutions at 25–95 °C

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HIGHLIGHTS

- Effects of temperature on the corrosion of LAS in simulated PWR water are studied.
- Increase of corrosion rate with increasing temperature in deaerated solution is observed.
- Corrosion rate peaks at approximately 75 °C in aerated solution.
- Deaeration decreases the corrosion rate in concentrated PWR water at 70–80 °C.
- Deaeration increases the corrosion rate in concentrated PWR water at 87.5–95 °C.

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ABSTRACT

The effects of temperature, solution composition and dissolved oxygen on the corrosion rate and electrochemical behavior of an A508III low alloy steel in boric acid solution with lithium hydroxide at 25–95 °C are investigated. In aerated solutions, increasing the boric acid concentration increases the corrosion rate and the anodic current density. The corrosion rate in deaerated solutions increases with increasing temperature. A corrosion rate peak value is found at approximately 75 °C in aerated solutions. Increasing temperature increases the oxygen diffusion coefficient, decreases the dissolved oxygen concentration, accelerates the hydrogen evolution reaction, and accelerates both the active dissolution and the film forming reactions. Increasing dissolved oxygen concentration does not significantly affect the corrosion rate at 50 and 60 °C, increases the corrosion rate at 70 and 80 °C, and decreases the corrosion rate at 87.5 and 95 °C in a high concentration boric acid solution with lithium hydroxide.

1. Introduction

Boric acid corrosion (BAC) at many pressurized water reactor (PWR) plants has been a concern of utilities for many years because of the potential leakage sources, such as flanged joints, valve packing, mechanical seals and fittings. In PWR plants, several components, such as reactor pressure vessels (RPV), valves, pumps, threaded fasteners and other structural parts, are constructed with carbon steels and low alloy steels (LASs) [1–5]. Such materials are usually not in direct contact with PWR primary water but could be exposed to primary water when stainless steel or nickel-based alloy corrosion resistant layers fail or as a result of leaks in valves and fittings, which can cause the contact of primary water with the external surfaces of carbon and low-alloy steel components. Under such conditions, the boric acid solution becomes concentrated due to evaporation and is aerated on contact with the environment, producing varying degrees of external corrosion of PWR components [2]. There have been several cases of corrosion of RPV materials by the leakage of primary water [6–10]. One instance was the discovery of a corrosion cavity (approximately 127 mm width, 178 mm long and through the LAS RPV head up to the stainless steel cladding) in the vessel head at the Davis-Besse Nuclear Power

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Station in March 2002 [11,12]. Most of the damage is thought to have occurred in the later stages and remained undetected for many months [13].

A533B and A508III LASs are often used as RPV materials and other key components in nuclear power plants. Several investigators [1–5,14,15] have conducted research and presented experimental data on the corrosion rates of carbon and LASs in boric acid solutions of varying concentrations and temperatures, aerated or deaerated, and under other test conditions. Argonne National Laboratory measured the electrochemical potential (ECP) and corrosion rates of RPV A533 steel and A508 steel in boric acid solutions under different operating conditions at temperatures of 95–316 °C [14]. The variations in test conditions, such as temperature, boric acid concentration, and dissolved oxygen, make correlations among the various sets of test results difficult, although it was clear that significant waste was possible under certain conditions [15]. A series of tests performed previously focused on high temperature and high pressure, similar to actual conditions. The temperature drops below 100 °C during normal shutdown of a nuclear power plant. High temperature/pressure condition and the condition below 100 °C are possible for the materials near or at a distance from the leaking sites. LiOH in primary water is almost eliminated under the normal shutdown condition, while LiOH would still exist in the leaking sites. Boric acid plus LiOH solutions are used to simulate the primary water leaking conditions. Concentrated solutions are used to simulate the results of evaporation after leakage. The effects of the boron concentration in conjunction with temperature and aeration on the corrosion rates were investigated by S. Fyfitch and H. Xu [15]. These researchers determined that the corrosion rates of LAS in concentrated boric acid solution increased sharply with increasing temperature in the range of temperature tested (21 °C–100 °C). The corrosion rate of A533B LAS varied between a few millimeters to tens of millimeters per year at 97.5 °C.

In the present work, the effects of temperature in conjunction with the solution composition and dissolved oxygen (DO) on the corrosion and electrochemical behavior of A508III LAS in boric acid solutions at temperatures from 25 to 95 °C were studied by weight loss measurements, electrochemical measurements and surface observations. Studying the corrosion and electrochemical behaviors of LAS in boric acid solutions would be helpful for understanding the fundamental factors and mechanism affecting the corrosion.

2. Experimental

The test material was an A508III LAS for RPVs in nuclear power plants. The chemical composition (wt. %) of the A508III steel used in this work is given in Table 1. Coupons of 15 × 13 × 2 mm with a 2 mm diameter hole for hanging were used for the corrosion weight loss measurements. The samples for electrochemical measurements were spot-welded to copper wires for electrical contact and were then mounted by epoxy with a 10 × 10 mm exposure area to the test solutions. Prior to measurements, the surfaces were ground mechanically with SiC paper up to 1000 grit and then rinsed using ethanol and acetone, respectively.

A solution containing 1200 ppm B in H_3BO_3 and 2 ppm Li in LiOH, called 1200 ppm-B/2 ppm-Li, was used to simulate the composition of normal PWR primary water. Throughout the text, adding B means adding H_3BO_3, and adding Li means adding LiOH. The solution with 6000 ppm B in H_3BO_3 and 10 ppm Li in LiOH was called 6000 ppm-B/10 ppm-Li solution, and the solution with 12000 ppm B in H_3BO_3 and 20 ppm Li in LiOH was called 12000 ppm-B/20 ppm-Li solution. These concentrated solutions were used to represent the local concentrated solutions near the leaking sites. In some cases, deionized pure water was used to study the effects of dissolved oxygen in solution. Test solutions were prepared using analytical grade reagents and pure water. Test temperatures varied from 25 to 95 °C under ambient pressure.

There is limited solubility of boric acid at ambient pressure. The solubility of boric acid at 25 °C is 5 g, which increases with increasing temperature; 12000 ppm B in H_3BO_3 cannot be dissolved in water at 25 °C. Weight loss tests were performed in three types of solutions: naturally aerated (without bubbling N_2 or O_2) and deaerated (with bubbling N_2) boric acid solutions with lithium hydroxide, and oxygenated pure water (with bubbling O_2). Bubbling N_2 or O_2 was used to investigate the effect of dissolved oxygen on the corrosion rates. Nitrogen or oxygen was supplied to the vessel 30 min prior to the immersion test and continued until the sample was immersed in the solution for 30 min. The surface films were analyzed using a scanning electron microscope (SEM). The solution volume to specimen area ratio was approximately 13.1 mL/cm^2. This ratio met the requirements of the standard ISO 11845:1995. The average corrosion rates V_{corr} (mm/y) were calculated by dividing the total weight loss by the immersion period. In most weight loss tests, the samples were immersed for 24 h in the test solutions. Some other immersion periods were used to determine the effect of immersion time on the corrosion rate. Three parallel samples were used for each test condition.

A three-electrode cell was used to study the electrochemical behavior of A508III steel. The working electrode was A508III steel, the counter electrode was a platinum plate and the reference electrode was a saturated calomel electrode (SCE) at room temperature of approximately 25 °C. All the potentials were measured and quoted against SCE except for the potential-pH (E-pH) diagram analysis. The measured potentials E_{SCE} (V_{SCE}) were converted to the standard hydrogen electrode (SHE) scale φ_e (V_{SHE}) by Eq. (1) [14]. The potentials vs. SHE are used in the E-pH diagrams.

$$\varphi_e = E_{SCE} + 0.242 - 7.6 \times 10^{-4} \Delta T \tag{1}$$

where ΔT is the temperature difference (in $^{\circ}$C) of the salt bridge in the reference electrode (i.e., the test temperature minus 25 °C). Potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) plots were measured using a Zahner-Zennium electrochemical workstation. Prior to polarization, the working electrode was immersed in the test solution for 30 min to reach a nearly stable open circuit potential (OCP). Anodic polarization curves were measured at a sweep rate of 1.67 mV/s from OCP to 1.5 V(SCE). Cathodic polarization curves were measured at a sweep rate of 0.33 mV/s from OCP to −1.1 V(SCE). EIS measurements were conducted at open circuit potentials in a frequency range from 1 MHz to 10 mHz at an AC amplitude of 10 mV. Each test was repeated three times and exhibited good reproducibility.

Table 1
Chemical composition of A508III steel (wt%).

Element	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Fe
Composition	0.216	0.228	1.39	0.012	0.0031	0.122	0.68	0.54	0.117	Bal