



# Influence of Conductivity on Corrosion Behavior of 304 Stainless Steel in High Temperature Aqueous Environment



Jiazhen Wang, Jianqiu Wang\*, En-Hou Han

Key Laboratory of Nuclear Materials and Safety Assessment, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

## ARTICLE INFO

### Article history:

Received 19 January 2015

Received in revised form

16 February 2015

Accepted 4 March 2015

Available online 14 December 2015

### Key words:

Stainless steel

Polarization

Electrochemical impedance spectra

High temperature corrosion

The influence of conductivity on corrosion behavior of 304 stainless steel (SS) in high temperature water was investigated by using in-situ potentiodynamic polarization curves, electrochemical impedance spectra (EIS) at 300 °C, and ex-situ scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The structures of oxide films formed on 304 SS change with different conductivities at 300 °C. With the increase in conductivity, the passive current density increases while the resistances of oxide films decrease. But the resistances do not decrease lineally with the increase in conductivity. A modified double-layer model for oxide structure was proposed to explain the influence mechanism of conductivity on the oxide films on 304 SS in high temperature water. Improving the <sup>10</sup>B enrichment level can reduce the conductivity of primary water and increase the corrosion resistance of 304 SS.

Copyright © 2016, The editorial office of Journal of Materials Science & Technology. Published by Elsevier Limited. All rights reserved.

## 1. Introduction

In all pressurized water reactors (PWRs), boric acid is used as a chemical shim to control excess reactivity in the fuel assemblies during a fuel cycle<sup>[1,2]</sup>. Although natural boric acid is normally used, only the <sup>10</sup>B isotope has a high capacity for thermal neutron capture by the following reaction<sup>[3,4]</sup>:



The injection of B in the typical ingredients of primary PWR coolant is 900–1800 ppm (by weight) as burnable neutron absorbers to control nuclear reactions. Besides, 2–5 ppm lithium hydroxide (LiOH) is also injected to achieve a desired pH range between 6.9 and 7.4, which minimizes the corrosion of structural materials, as well as the solubility and transport of activated corrosion products<sup>[1,5]</sup>.

In support of advanced fuel management trends, a higher <sup>10</sup>B content is required at the beginning of the fuel cycle. About 80% of total B in nature exists in the form of <sup>11</sup>B isotope, which is essentially useless as a neutron absorber<sup>[1,3,6]</sup>. Moreover, <sup>11</sup>B isotope increases the total concentration of required boron acid (H<sub>3</sub>BO<sub>3</sub>) to obtain a target <sup>10</sup>B isotope content<sup>[7,8]</sup>. However, increasing boron concentration brings many difficulties associated with the need to

increase the concentration of LiOH in primary PWR to maintain the relative stability of pH values. The increased levels of H<sub>3</sub>BO<sub>3</sub> and LiOH concentration, along with the rise of subsequent conductivity, aggravate the boron deposition on fuel and accelerate the corrosion rates of fuel cladding and Alloy 600<sup>[1,2,4,6]</sup>.

Because the corrosion of alloys in high temperature water is an electrochemical process in nature, a large number of studies have investigated the influences of temperature<sup>[9–12]</sup>, pH value<sup>[11,13,14]</sup>, dissolved oxygen (DO)<sup>[15]</sup> and dissolved hydrogen (DH)<sup>[16]</sup> on electrochemical characters of the alloys by in-situ electrochemical measurement techniques in high temperature water. However, few studies focus on how conductivity influences the corrosion behavior of stainless steels (SS) and nickel-based alloys in high temperature water. Liu et al.<sup>[14]</sup> investigated the influence of pH on the corrosion behavior of 316L SS at 300 °C, and found that the corrosion rate of 316L SS reduced with the increase of pH value. However, the pH and conductivity of the experimental solutions changed at the same time, and the influence of conductivity on corrosion behavior of 316L SS was not discussed.

Thus, the main purpose of the present work is to study the effect of conductivity on corrosion behavior of 304 SS in high temperature aqueous environments by means of in-situ potentiodynamic polarization, electrochemical impedance spectra (EIS), ex-situ scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analysis. One duplex-layer model is proposed to understand the evolution process of oxides on 304 SS in high temperature aqueous solutions with different conductivities.

\* Corresponding author. Ph.D., Prof.; Tel.: +86 24 23893723; Fax: +86 24 23894149. E-mail address: [wangjianqiu@imr.ac.cn](mailto:wangjianqiu@imr.ac.cn) (J. Wang).

## 2. Experimental Procedures

### 2.1. Samples and solutions

The composition (wt%) of 304 SS used for this work is 18.65 Cr, 9.27 Ni, 1.88 Mn, 0.035 C, 0.66 Si and Fe balance. The material was solution annealed at  $1100 \pm 3$  °C for 1 h and then water quenched. The samples with a size of  $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$  were used for electrochemical experiments and were carefully ground with SiC papers up to 2000 grit. After that, all the samples were polished with  $3.5 \mu\text{m}$  diamond paste. The samples were subsequently welded to 316 SS wires shielded with heat-shrinkable polytetrafluoroethylene tubes. There are three parallel electrochemical samples in each electrochemical experiment and another two parallel samples for SEM, XRD and XPS analysis. The autoclave was connected with a re-circulation loop, and the water chemistry parameters were monitored online, including DO, DH, pH value and electrical conductivity. The DO and DH values were automatically controlled and adjusted using software LabView 8.5. The control error was lower than 1%. The autoclave and re-circulation loop were pre-oxidized in the relevant testing solution before the formal experiment. The testing electrolytes were four kinds of lithiated and borated solutions in the high-purity deionized water (conductivity:  $18.25 \text{ M}\Omega \text{ cm}$ ). The concentrations of B and Li, the pH values, and conductivities of the solutions at 300 °C are listed in Table 1. All the data in the table have been calculated using commercial software pHSC4 from Duke Power Company. The testing solution was first deaerated by continuously bubbling with  $\text{N}_2$  gas (99.99%) until the DO was less than 0.01 ppm, and then inflated with  $\text{H}_2$  gas (99.999%) until the DH reached 2.3 ppm. The samples were immersed in  $300 \pm 1$  °C and 10 MPa high temperature water in a 2 L Ni-lined stainless steel autoclave for 72 h.

### 2.2. Electrochemical measurements

A Gamry Reference 600 Potentiostat and corresponding software were used for all electrochemical measurements. The three-electrode system including working, counter and external Ag/AgCl reference electrodes were used. The counter electrode was a platinum foil with a size of  $20 \text{ mm} \times 20 \text{ mm}$ , and the concentration of KCl in the Ag/AgCl reference electrode was 0.1 mol/L. Prior to the heating process of autoclave, the samples were reduced potentiostatically at  $-1.0 \text{ V}$  (vs SHE—standard hydrogen electrode) for 10 min to remove the surface oxides on SS and then kept in the solution at  $300 \pm 1$  °C for 72 h. According to the American Society for Testing and Materials F2129 Standard and Ref.<sup>[17,18]</sup>, 72 h of pre-oxidation could allow the extent of oxide films achieved, and the open circuit potential (OCP) could reach the quasi-steady condition at the same time.

The OCPs of 304 SS in testing solutions at 300 °C were measured at intervals. The EIS measurements were performed at OCP. The alternating current signal amplitude was  $\pm 10 \text{ mV rms}$  and the frequency ranged from 100 kHz to 10 mHz. The potentiodynamic

**Table 1**  
Contents of different solutions and the corresponding pH values and conductivities at 300 °C

Solution	B (ppm)	Li (ppm)	pH 300 °C	Conductivity 300 °C ( $\mu\text{S/cm}$ )
1#	0	0.56	7.29	113.88
2#	50	0.72	7.29	125.31
3#	200	1.24	7.29	164.34
4#	480	2.3	7.29	242.64

Note: pH 300 °C and conductivity 300 °C of testing solutions are calculated by a commercial software pHSC4.

polarization experiments were performed at a scanning rate of 0.5 mV/s starting from  $-0.1 \text{ V}$  vs OCP. A Gamry Echem Analyst Software was used for calculating the fitting results of EIS.

All the potentials have been converted into SHE by the following equation<sup>[19]</sup>:

$$E_{\text{SHE}} = E_{\text{obs}} + 0.2866 - 0.001 \times (T - T_r) + 1.745 \times 10^{-7} \times (T - T_r)^2 - 3.03 \times 10^{-9} \times (T - T_r)^3 \quad (2)$$

where  $E_{\text{SHE}}$  is the electrode potential vs SHE,  $E_{\text{obs}}$  is the measured electrode potential,  $T_r$  is room temperature (25 °C), and  $T$  is the measured experimental temperature (300 °C).

### 2.3. Analysis of surface film

To observe the microstructure of corrosion product on the surface of 304 SS, an FEI XL30 field emission environmental scanning electron microscope (ESEM) was used. The phases of oxide films on 304 SS after immersion were identified using a PANalytical X'Pert Powder X-ray diffraction (XRD), with  $\text{AlK}\alpha$  radiation. The generator voltage and tube current were 40 kV and 40 mA, respectively. The scanning range of the detector was from  $10^\circ$  to  $90^\circ$ , the step size was  $0.05^\circ$ , and the time per step was 0.8 s. XPS analysis was performed using a VG ESCALAB 250 X-ray photoelectron spectrometer. Composition-depth profiles were obtained with 2.0 keV Ar ions at a target current of  $2.0 \mu\text{A/cm}^2$ . The sputtering rate was estimated to be about 0.1 nm/s (vs  $\text{Ta}_2\text{O}_5$ ). To characterize the thickness of oxide film qualitatively, the equivalent oxide thickness is defined from the XPS depth profiles where the atomic percent of O reaches 10%.

## 3. Results

### 3.1. Change of OCP and potentiodynamic polarization curves

Fig. 1 shows the evolution of OCPs for 304 SS in different solutions at 300 °C. The OCPs of 304 SS reduce with the increase of B and Li injection. The OCP values of 304 SS in 1#, 2#, 3# and 4# solutions are  $-0.594$ ,  $-0.625$ ,  $-0.673$  and  $-0.685 \text{ V}$ , respectively.

Fig. 2 shows the potentiodynamic polarization curves for 304 SS after 72 h in different concentrations of B and Li solutions at 300 °C. All the passive potentials of 304 SS are nearly located around  $-0.4 \text{ V}$ , which can be due to the transformation of Fe–Cr oxides into Ni–Fe oxides based on the  $E$ –pH diagram<sup>[20–23]</sup>. The anodic current density, the cathodic current density and the passive current density all increase with the rise of conductivity. The passive current density

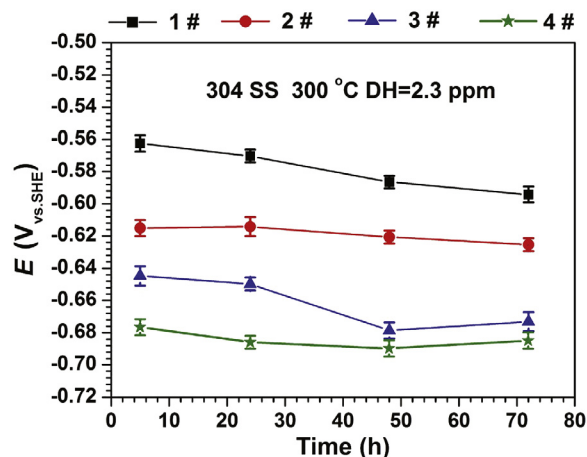


Fig. 1. Evolution of OCP for 304 SS in different solutions at 300 °C.

Download English Version:

<https://daneshyari.com/en/article/1555926>

Download Persian Version:

<https://daneshyari.com/article/1555926>

[Daneshyari.com](https://daneshyari.com)