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Evaluation of temperature effect on the corrosion process of 304 stainless steel in high temperature water with electrochemical noise

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ABSTRACT

The effect of temperature on corrosion process of 304 stainless steel (SS) in high temperature water was investigated by electrochemical noise (EN), scanning electron microscope (SEM), Raman spectrum and X-ray photoelectron spectroscopy (XPS). The experimental results showed that the corrosion process could be divided into two stages (passivity and active dissolution) with the increasing temperature. At 100 °C, the oxide film was a single layer mainly consisting of Cr_2O_3. However, at 250 °C, it became a double layer with an inner layer of Cr–Fe spinel compound and an out precipitated layer. The related growth mechanisms of the oxide film were also discussed.

1. Introduction

The stainless steel (SS) grade 304 is widely used as piping materials in the secondary circuit of nuclear power plants due to its superior mechanical properties and corrosion resistance [1,2]. However, some localized corrosion problems, such as pitting corrosion, intergranular corrosion and stress corrosion cracking [2], can still be observed in 304SS in the pressurized water reactors (PWR), which could cause the potential dangers of safety and integrity of nuclear power plants.

Since the corrosion degradation of stainless steel in high temperature water is an electrochemical process in nature, the effect of immersion time [3], pH value [4], dissolved oxygen [4], and temperature [5] on the corrosion behavior of stainless steel or nickel based alloys has been investigated by ex-situ electrochemical techniques, such as potentiodynamic polarization [3,4], electrochemical impedance spectra (EIS) [3–5] and Mott–Schottky plots (MS) [6], and surface characterization methods, such as X-ray photoelectron spectroscopy (XPS) [7,8], scanning electron microscopy (SEM) [7–9] and transmission electron microscopy (TEM) [9]. However such electrochemical techniques are time-consuming and need to be operated under an external potential/current input signals, which may disturb the experimental system. In order to detect the corrosion processes of stainless steel in subcritical environments without any external disturbance, electrochemical noise (EN) provides a better way.

EN method is an in-situ electrochemical technique, which measures the spontaneously generated potential and current fluctuations during the corrosion process and does not disturb the corrosion system [10,11]. Therefore, EN technique has gained popularity in the recent years and emerged as a promising technique for corrosion monitoring. Besides, EN technique has been used successfully in the high temperature water environment to study the effect of flow rate on the corrosion rate of 304SS at high temperature [12], the correlation between noise resistance and polarization resistance of 08CH18N10T estimated from impedance spectra in the absence and presence of Cl^- at 280 °C [13], the susceptibility of Alloy 600 to intergranular stress corrosion cracking (IGSCC) in simulated primary water chemistry [14], and the initiation and propagation of Pb-assisted stress corrosion cracking (PbSCC) of Alloy 600 at 290 °C [15]. However, only few studies concerned the corrosion process and mechanism of 304SS by the method of EN in high temperature water.

The objective of this work was to explore the effect of temperature on the corrosion process of 304SS in high temperature water using in-situ EN technique combined with ex-situ techniques such as SEM, Raman spectrum and XPS. Besides, the growth mechanisms of oxide film formed on 304SS in high temperature were also discussed.

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2. Experimental

2.1. Materials and electrolyte

The chemical composition of 304SS used in this work was 0.035%C, 0.66%Si, 2.00%Mn, 18.65%Cr, 9.27%Ni, 1.00%Cu and Fe balance. Samples for EN test (Φ6 mm × 25 mm) and surface characterization (5 mm × 5 mm) were cut from 10 mm thick plates, which have been solution annealed at a temperature ranging from 1050 °C to 1150 °C. Before experiments, the samples were mechanically abraded by water emery papers up to #2000 successively and degreased with ethanol.

The solution used in this work was 1500 ppm (μg/g) B as H_3BO_3 and 2.3 ppm (μg/g) Li as LiOH. This solution is used to simulate the prevailing environment of PWR. The experiment was performed at the temperature of 100, 150, 200, 220 and 250 °C under their balance pressures respectively (see Table 1). The pH value of the neutral solution and test solution at each experimental temperature is shown in Table 2. After experiments, the test samples were rinsed with distilled water and ethanol, and then dried in air for surface characterization.

2.2. Electrochemical noise measurement

Fig. 1 presents a schematic of the autoclave and the EN experiment. The EN measurement was carried out by an Autolab 302N electrochemical workstation through a zero resistance ammeter (ZRA). The exposed area of the working electrode was approximately 5 cm^2. In the absence of other redox couples, Pt electrode quickly assumes the equilibrium O_2/H_2O or H_2O/H_2 potentials. The electrochemical current noise (ECN) between two specimens of the pair kept at the same potential and the electrochemical potential noise (EPN) versus the reference were monitored simultaneously. Each set of EN records, containing 1024 data points, was recorded with a data-sampling interval of 0.5 s. EN data was recorded with time for 25,600 s. Fifty time records were analyzed for each temperature.

2.3. Electrochemical noise analysis

2.3.1. Noise resistance analysis

The noise resistance R_n was obtained by equation $R_n = \sigma_V/\sigma_I$, where σ_V is the standard deviation of the values of EPN and σ_I is the standard deviation of the values of ECN.

2.3.2. Shot noise analysis

According to the shot noise theory [16,17], the corrosion process is produced by a series of 'event' of short duration and constant charge. Based on this theory the average frequency f_n in the corrosion events is calculated by equation $f_n = B^2/\mathrm{PSD}_E A$, where PSD_E is the low frequency PSD values of the EPN.

2.3.3. Principal component and cluster analysis

The group results as the function of time and temperature are shown in Table 3. Nine statistical parameters, i.e., *mean value*, *standard deviation*, *skew*, *kurtosis* as well as *noise resistance* were selected for the principal component analysis of EN data. Table 4 shows the calculated results for all these nine parameters. Parameters (σ_V, σ_I, I_{mean}, R_n) with the weight value larger than 0.8 were determined for further cluster analysis. Both the principal component and cluster analysis were calculated by the SPSS software. More details of principal component and cluster analysis procedure can be found in Refs. 18,19.

2.3.4. Wavelet analysis

The EPN was decomposed to eight levels ($d1$–$d8$, and $s8$) using the wavelet transform technique based on orthogonal db4 wavelet [20,21]. Sometimes the contribution of the smooth $s8$ coefficients to the overall signal is too large to shelter the information about D series crystals [23], therefore the fraction of energy associated with each detail crystal (E_j^d) is calculated as follows:

Table 1
Experimental temperatures and their balance pressures applied in the test.

Temperature (°C)	100	150	200	220	250
Pressure (MPa)	0.1	0.4	1.5	2.2	3.7

Table 2
The pH of neutral solution and test solution at experimental temperatures.

Temperature (°C)	100	150	200	220	250
pH (neutral solution)	6.16	5.82	5.62	5.58	5.57
pH (test solution)	6.15	6.16	6.21	6.27	6.41

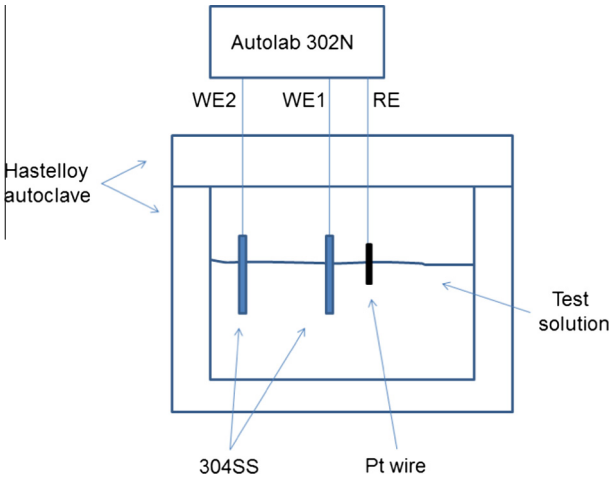

Fig. 1. Schematic diagram of the autoclave and electrode system.

Table 3
The grouping results for cluster analysis.

Temperature (°C)	Case	Group
100	1–50	1
150	51–100	2
200	101–150	3
220	151–200	4
250	201–250	5

Table 4
Factor loadings in the three principal components of EN data analysis.

Variable	Component 1	Component 2	Component 3
V_{mean}	0.356	0.662	−0.02
σ_V	0.959	0.007	−0.067
V_{skew}	−0.038	0.547	0.434
V_{kurt}	0.036	0.52	0.512
I_{mean}	0.933	0.019	0.088
σ_I	0.899	−0.164	−0.077
I_{skew}	0.15	−0.487	0.68
I_{kurt}	0.067	0.297	−0.583
R_n	−0.924	0.062	0.007