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Short Communication

Corrosion Behavior of SS-304 in NaCl Solution at Different Temperatures Using Electrochemical Noise Technique

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Corrosion behavior of 304 stainless steel(SS-304) exposed to 2mol/L NaCl solution at different temperatures(20 ^{0}C, 40 ^{0}C, 60 ^{0}C, 80 ^{0}C) has been studied using electrochemical noise(EN). EN data were analyzed by statistical theory, shot noise theory and wavelet analysis theory. Noise resistance(R_n) and shot noise analysis results showed that the corrosion rate of SS-304 also increased as temperature increased, but the degree of corrosion rate increasing was different obviously during different temperature ranges. In addition, increasing temperature changed the corrosion type of SS-304 from passivation to pitting. Wavelet analysis provided more details about the corrosion process. The analysis results showed that at 20 ^{0}C SS-304 would experience passivation and metastable pitting process for a long time. When temperature increased to 40 ^{0}C, 60 ^{0}C and 80 ^{0}C, passivation and metastable pitting process got shorter greatly, which may be caused by the change of passivation film property and the acceleration of electrochemical reaction at high temperature. Finally, the EN analysis results were verified by the corrosion morphologies obtained from optical microscope.

Keywords: SS-304; Electrochemical Noise; pitting corrosion; high temperature; Wavelet analysis

1. INTRODUCTION

SS-304 has been widely used as construction materials in many industries due to good corrosion resistance ability. However in some corrosive environment, local corrosion still can occur on SS-304 due to the corrosion of chloridion, which may shorten the equipment life. Now SS-304 has more chances to be applied in relatively high temperature environment, such as nuclear power industry, chemistry industry[1]. Temperature has a great effect on the corrosion behavior of SS-304 exposed to the chloridion environment[2]. Generally as temperature increases, local corrosion occurs more easily and propagates faster, which can accelerate the failure of equipment greatly. Even so, compared with the corrosion study of SS-304 at room temperature, the corrosion study at relatively high temperature is too scarce in the literatures[3]. Therefore it is necessary to study corrosion behavior of SS-304 in corrosive environment at relatively high temperature.

EN method is defined as the fluctuations of potential and current generated spontaneously during the corrosion process[4]. EN method has some obvious advantages compared with polarization, electrochemical impedance spectroscopy and other electrochemical methods[5,6]. EN is able to instantaneously monitor the corrosion rate; EN is carried out without an artificial disturbance of the system; EN can provide more information to research corrosion mechanism. In addition, EN method has been widely used to study the corrosion behavior of SS-304 at room temperature. Many researchers have gained a lot of achievements. Li Liu studied the pitting mechanism of stainless steel in NaCl solution with EN method and AFM analysis[7]. Bing Zhao studied the corrosion behavior of reinforcing steel exposed in chloride solution by analyzing EN data with wavelet analysis method[8]. Cottis found that EN data can be processed by shot noise theory to distinguish different corrosion types[9]. These corrosion achievements with EN method at room temperature can provide us reference for our corrosion study of SS-304 at relatively high temperature, which may benefit us greatly. Although EN method has so many advantages, EN method was rarely used to study corrosion of SS-304 at relatively high temperature. Therefore, more attention still needs to be focused on using EN method to study corrosion of SS-304 at relatively high temperature.

The aim of this paper is characterization the corrosion behavior of SS-304 exposed to 2mol/L NaCl solution at different temperatures(20 ^{0}C, 40 ^{0}C, 60 ^{0}C, 80 ^{0}C) using electrochemical noise technique. Firstly, the EN data were measured simultaneously for 12 hours at 20 ^{0}C, 40 ^{0}C, 60 ^{0}C and 80 ^{0}C. Secondly, the EN data were analyzed by statistical theory, shot noise theory and wavelet analysis theory to evaluate corrosion behavior of SS-304 at different temperatures.

2. EXPERIMENT

The specimen used in this study was SS-304(chemical composition, in mass fraction, %: C≤0.080%; Cr 18.0%-20.0%; Ni 8.00%-11.0%; Mn≤ 2.0%; Si≤1.0%; P≤0.045%; S≤0.03%; Fe, balance).From the SS-304 plates, 10mm×10mm×3 mm specimens were cut, then the specimens were mounted in epoxy with only the working electrode surface of 1cm^2 exposed. The exposed surface was grinded using abrasive papers through 500-grade to 3000-grade, polished with diamond paste, rinsed using acetone, degreased with deionized water and dried in air. The test medium used in experiments was 2 mol/L NaCl solution, which was prepared by the analytical-grade reagents and distilled water. The solution was heated by Constant Temperature Baths.

The electrochemical potential noise and electrochemical current noise were measured simultaneously through a zero resistance ammeter (ZRA) mode via a data acquisition system working as a multi-channel electrochemical workstation. This system is constructed by NI-CRIO and developed software. A conventional three-electrode cell was used for the experiments. The working electrode and counter electrode were the same 304 specimens and the reference electrode was Pt wire. Unlike saturated calomel electrode, as temperature increased, Pt wire was still stable.

In this passage, noise resistance(R_n), shot noise and wavelet method were used to process EN data. Now noise resistance(R_n) defined as the ratio of the standard deviations of the potential(σ_E) and current noise(σ_I) was widely used to reflect corrosion rate[5]. In shot noise theory, it is well known that the parameters q and f_n can provide vital information for understanding the mechanism of the corrosion processes. Generally, q can represent the mass of the metal lost in events, meanwhile f_n provides information about the corrosion rate [9]. Q and f_n can be estimated from the following equations based on the shot-noise theory [10].

$$I_{corr} = q \times f_n \tag{1}$$

$$q = \frac{\sigma_I \sigma_E}{Bb} \tag{2}$$

$$f_n = \frac{I_{corr}}{q} = \frac{B^2 b}{\sigma_E^2} \tag{3}$$

where I_{corr} is the average corrosion current, σ_I andσ_E are the standard deviation of the current noise and potential noise, b is the range of measurement of the experiment, B is the Stern-Geary coefficient.

EN data were recorded at different temperatures(20 ^{0}C, 40 ^{0}C, 60 ^{0}C and 80 ^{0}C) during 12 hours. The sampling interval in experiment is 0.2s. EN data were divided into one hundred and five time records. Each data record contains 2048 data points. The data processing was implemented by Matlab2013 and the figures were drawn by origin 8.5.

3. RESULTS AND DISCUSSION

3.1 Noise resistance(R_n) analysis

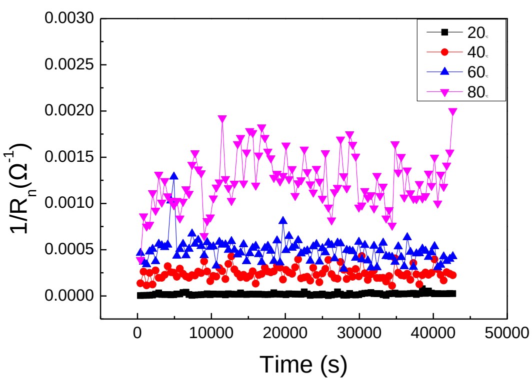

Figure 1. The reciprocal of noise resistance($1/R_n$) of SS-304 at 20 ^{0}C, 40 ^{0}C, 60 ^{0}C and 80 ^{0}C

Fig 1 shows the the reciprocal of noise resistance($1/R_n$) with immersion time at different temperatures. In Fig 1, it was observed that as temperature increased, $1/R_n$ also increased, which indicated that corrosion rate increased with increasing temperature. In addition, as temperature increased to 80 ^{0}C, corrosion rate and the volatility of corrosion rate got larger obviously, which may be caused by the instability of electrochemical reaction at high temperature.

3.2 Shot noisy analysis

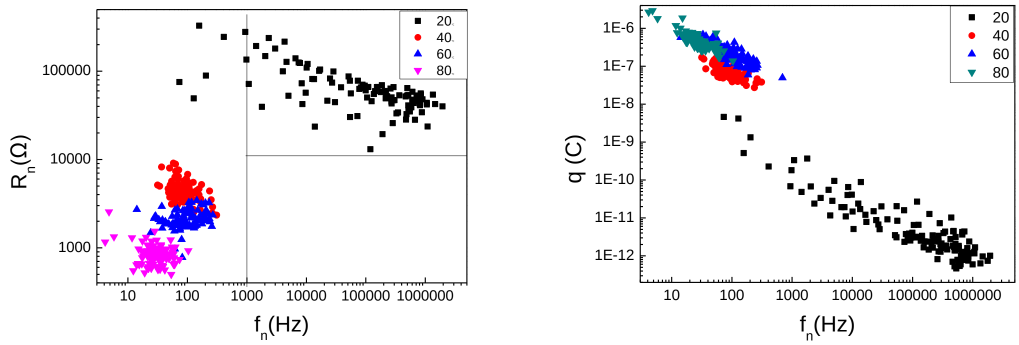

Figure 2. a) Plot of a) f_n *vs* q and b) f_n *vs* R_n for different temperatures in 2 mol/L NaCl solution

According to Cottis[11], the f_n *vs* R_n graph can be used to distinguish different corrosion types. The graph can be divided into three regions. The region with high frequency and low resistance indicates general corrosion. The region with high frequency and high resistance is associated with passivation. And the last region with low frequency denotes pitting corrosion.

In Fig. 2a, it was found that the points at 20 ^{0}C mainly focused on the passivation region with high frequency and high resistance, meaning that the dominant process at 20 ^{0}C was passivation. Meanwhile a few points exist in pitting region, which meant that pitting corrosion has a tendency to occur on SS-304 and passivation may be the first stage of pitting process. As temperature increased to 40 ^{0}C, 60 ^{0}C, 80 ^{0}C, the points shifted from passivation region to pitting corrosion region, which meant the susceptibility of SS-304 to pitting corrosion increased and the development of pitting accelerated greatly with the increasing temperature. This was also in an agreement with the result of theoretical analysis. Electrochemical reaction between passivation film and chloridion accelerated increasing temperature. Once passivation film ruptured, chloridion can contact SS-304 directly, leading to the local priority corrosion. Therefore the increasing temperature promoted electrochemical reaction, resulting in the acceleration of pitting development.

Fig. 2b shows the plot of f_n *vs* R_n for different temperatures in 2 mol/L NaCl solution. It was noted that as the temperature increased, the q values increased whereas f_n values decreased, which suggested an increased tendency to undergo pitting corrosion with increase in the temperature. It was also observed that the q and f_n values at 20 ^{0}C were far less than q and f_n values at 40 ^{0}C, 60 ^{0}C and 80 ^{0}C. The q and f_n values between 40 ^{0}C and 60 ^{0}C seemed a little similar and difficult to distinguish, especially f_n values. When temperature increased to 80^{0}C, the q and f_n values have an obvious increase again. This change showed that the corrosion rate of SS-304 at different temperatures can be divided into three stages. Firstly corrosion rate at 20^{0}C was very small; When temperature increased to 40 ^{0}C and 60 ^{0}C, the corrosion rate increased obviously. But the distinction of corrosion rate between 40 ^{0}C and 60 ^{0}C seemed a little fuzzy; When temperature increased to 80 ^{0}C, corrosion rate has an obvious increase again, which was in an agreement with the R_n analysis result.

3.3 Wavelet analysis

In wavelet analysis theory, energy distribution plots(EDP) have been widely used in analyzing corrosion process and corrosion mechanism. Generally EN data was divided into different crystals according to frequency. The energy of each crystal was calculated. Li Liu and Zhao Bing[7,8] found that the crystal occupying maximum energy among all crystals can reflect corrosion process. The d1 and d2 crystal can represent passivation process. The d3–d5 crystals mean the breakdown and repassivation of the passivation film of stainless steel, corresponding to metastable pitting corrosion process. The d6-d8 crystals can represent the diffusion process, corresponding to the development of stable pitting. In this passage, db4 wavelet was used for 7 levels of wavelet decomposition

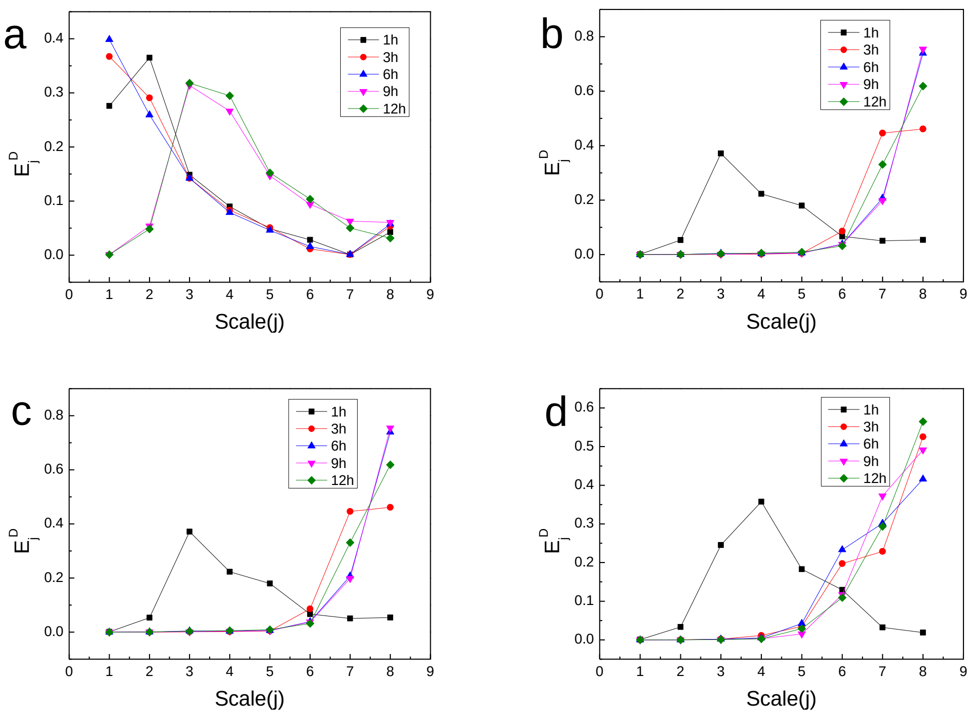

Figure 3. EDP of current noise of during different immersion periods at a) 20^{0}C b) 40^{0}C c) 60^{0}C d) 80^{0}C

Fig. 3 shows the energy distribution plots(EDP) of current noise at different time and different temperatures. In Fig. 3a, it was noted that d1 and d2 crystals occupied the main energy at 1h, 3h and 6h, which meant that SS-304 mainly experienced passivation process during the first 6h. When immersion time increased to 9h and 12h, d8 became the maximum energy, indicating that metastable pitting has taken place. In Fig. 3b, c, d, it was observed that the EDP at 40 ^{0}C, 60 ^{0}C,80 ^{0}C has similar characteristic. At the beginning of experiment, d3 crystal was the maximum energy. When immersion time increased to 3h, 6h, 9h and 12h, d8 crystal became the maximum energy. This showed that at the first hour of experiment, metastable pitting was dominant. When immersion time increased to 3h, 6h, 9h and 12h, the diffusion process corresponding to the development of stable pitting became dominant process. Compared with the pitting corrosion process at 20 ^{0}C, the passivation and metastable pitting process got shorter greatly, which may be caused by the change of passivation film and the acceleration of electrochemical reaction at high temperature.

3.4 Physical corrosion characterization

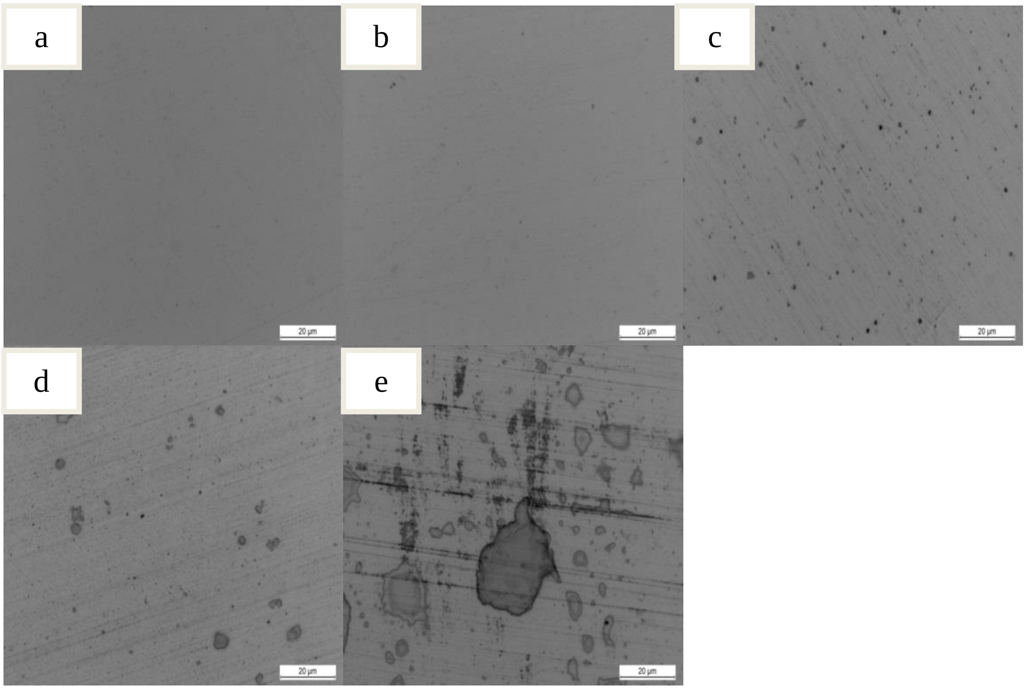

Figure 4. Optical images of SS-304 a) prior to exposure in NaCl solution and after exposure in NaCl solution for 12h at b) 20 ^{0}C c) 40 ^{0}C d) 60 ^{0}C and e) 80 ^{0}C

Fig. 4a shows the optical images of SS-304 after exposure in NaCl solution for 12h at 20 ^{0}C, nearly the same with original morphology, which meant that stable pits did not occur. Fig. 4b, c present many small pits, which meant SS-304 has formed stable pits. Compared with the sample surface morphology at 40 ^{0}C, the sample surface at 60 ^{0}C seemed smoother. This is because stable pits can act as local anodes and protect the area around them against pitting corrosion [12]. Fig. 4d shows many much larger pits than the pits generated at 40 ^{0}C and 60 ^{0}C, which implied that the high temperature increased the pitting corrosion rate greatly.

4. CONCLUSIONS

(1) The corrosion rate of SS-304 at different temperatures can be divided into three stages. Firstly corrosion rate at 20 ^{0}C was very small; When temperature increased to 40 ^{0}C and 60 ^{0}C, the corrosion rate increased obviously. But the distinction of corrosion rate between 40 ^{0}C and 60 ^{0}C seemed a little fuzzy; When temperature increased to 80 ^{0}C, corrosion rate has an obvious increase again.

(2) The rise in temperature changed the corrosion types. At 20 ^{0}C, the main corrosion process may correspond to passivation. However, when temperature increased to 40 ^{0}C or above, pitting corrosion became the dominate corrosion type.

(3) Wavelet analysis provided a lot of details about pitting corrosion process. At 20 ^{0}C SS-304 would experience passivation and metastable pitting process for a long time. When temperature increased to 40 ^{0}C, 60 ^{0}C and 80 ^{0}C, passivation and metastable pitting process got shorter greatly.

(4) A good relationship between the EN analysis results and the corrosion morphologies has been observed during the corrosion process of SS-304 in NaCl solution at different temperatures.

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