



Corrosion initiation of stainless steel in HCl solution studied using electrochemical noise and in-situ atomic force microscope

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ABSTRACT

An in-situ atomic force microscope (AFM), optical microscope and electrochemical noise (ECN) techniques were applied to the investigation of corrosion initiations in an early stage of 1Cr18Ni9Ti stainless steel immersed in 0.5 M HCl solution. The electrochemical current noise data has been analyzed using discrete wavelet transform (DWT). For the first time, the origin of wavelet coefficients is discussed based on the correlation between the evolution of the energy distribution plot (EDP) of wavelet coefficients and topographic changes. It is found that the occurrence of initiation of metastable pitting at susceptible sites is resulted from the reductive breakdown of passive film of stainless steel in the diluted HCl solution. The coefficients d_4 – d_6 are originated from metastable pitting, d_7 represents the formation and growth of stable pitting while d_8 corresponds to the general corrosion.

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1. Introduction

Stainless steel is a versatile material that is frequently utilized in various corrosive environments. The corrosion initiation process of stainless steel has aroused a great deal of attention in the last few decades because the corrosion initiation is very complicated and it may cause various types of localized corrosions. Stewart and Williams conducted a detailed analysis of the influence of MnS on pitting initiation process, and confirmed that the inclusions dominated as pitting nucleation sites [1]. Renner et al. employed AFM to observe the topographical characteristics of initial corrosion on the atomic scale under different potentials [2]. Wang and Li used electronic speckle pattern interferometry (ESPI) to study the initial corrosion of stainless steel [3]. Their previous studies mainly focused on the mechanism of initial pitting. However, little work about the corrosion initiation of stainless steel in a dilute HCl solution can be found in the literature.

The electrochemical noise (ECN) technique has been developed as a powerful technique in corrosion studies. It has been extensively used for the in-situ detection of spontaneous changes in localized corrosion processes, in particular pitting, cavitation attack, stress corrosion cracking or corrosion under coatings. This is made possible by measuring the fluctuations of the current and potential simultaneously, which are generated during the corrosion process

[4–8]. Electrochemical noise analysis has also been widely used for the in-situ characterization and monitoring of corrosion processes of various systems, and it offers some advantages over the common electrochemical techniques. They are [9]: (1) very fast measurements enable the user to register and monitor the corrosion process instantaneously; (2) sensitivity to the early initiation process of localized corrosion, unlike conventional techniques that provide little information [10]; (3) possibility to be used without disturbing the system under investigation [11]; (4) a potential in-situ tool to monitor the corrosion stages of constructional engineering.

The sensitivity of ECN measurement to localized corrosion is much higher than that of the traditional techniques. However, the data analysis of ECN remains difficult. Many methods have been developed to analyze the ECN data, including statistical analysis [12–15] and spectral analysis [16–20]. The most commonly used ECN analysis methods (statistical and spectral) are devised for stationary signals that do not show distinctive transients. The main disadvantage of those methods is that they analyze signals by averaging the features across the whole time record. Transient information may be lost in this analysis process.

Wavelet transform (WT), especially discrete wavelet transform (DWT), has been proposed as an alternative tool to overcome the limitations of traditional methods in the analysis of non-stationary signals of ECN data [21–23]. WT or DWT can provide information about transients in both time and frequency domain. Moreover, it is possible to work with non-stationary signals, so it has been used to differentiate corrosion types and to study corrosion mechanism. Using the wavelet transform method, the ECN data can be decomposed to different wavelet coefficients with corresponding time

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Table 1

The component of 1Cr18Ni9Ti stainless steel.

C (≤(%))	Si (≤(%))	Mn (≤(%))	P (≤(%))	S (≤(%))	Ti (≤(%))	Cr	Ni	Fe
0.12	1.00	2.00	0.035	0.30	0.98	17.00–19.00	8.00–11.00	Balance

scales [20–22], which are associated with different electrochemical transient events. Aballe et al. introduced the energy distribution plot (EDP) to monitor the fluctuation of transient events [21,22]. Qiao and Ou and Zhao et al., respectively employed EDP to analyze the ECN of Q235 carbon steel in cement mortar [23,24]. However, the corresponding corrosion event of each wavelet coefficient is still unclear.

In this work, the corrosion initiation of 1Cr18Ni9Ti stainless steel in dilute HCl solution was studied using an in-situ AFM, optical microscope and electrochemical noise. An attempt was made to verify the origin of electrochemical current noise using the correlation between the corrosion morphologies and the wavelet coefficients.

2. Experimental

The chemical composition of 1Cr18Ni9Ti stainless steel used in this work is listed in Table 1. The samples were prepared and embedded in epoxy resin. The working surface was polished with 400, 800, 1200 and 1500 grit silicon carbide paper and 1 μm alumina powder. The polished samples were ultrasonically cleaned in acetone and ethanol.

The ECN was measured using EN500 electrochemical noise and galvanic corrosion monitor (Wuhan Corrtest Instrument Co., Ltd.). Two identical stainless steel electrodes were used as working electrodes to measure electrochemical current noise. Both of them were buried in epoxy with two square faces of 1 mm × 1 mm exposed as the working surface. The polished electrode was mounted to a cell, which was designed to execute the ECN measurement and in-situ optical microscope detector synchronously. The electrochemical noise data recording started immediately after the solution was added to the cell. The sampling time of each ECN measurement was set to 1024 s with a frequency of 2 Hz. In order to record the current noise in 9 h of immersing time, the ECN measurement was executed continuously 30 times. DWT was employed to analyze the ECN data in this work; Aballe et al. had described its background [21,22]. By using DWT, the electrochemical current noise data was decomposed into two kinds of coefficients: (1) the smooth coefficient, s_8 , which contains information about the general trend of the signal; (2) the detail coefficients, $d_j = (d_1, d_2, \dots, d_8)$, which contains information about the local fluctuations in the signal. Each set of coefficients d_1, d_2, \dots, d_8 and s_8 is called a crystal. Transients with different time scales are attributed to the detail coefficients, d_1 – d_8 , whose time scales are shown in Table 2. The slowest processes represented by s_8 are the principal part of the dc trend. They are attributed to general process, or the asymmetry between two working electrodes, which usually contains most of the signal's energy. In order to eliminate the dc trend influence, the energy of s_8 will not be considered in this paper when plotting the EDP of wavelet coefficients.

The in-situ AFM measurement was performed using UltraObjective Nanostation III (SIS GmbH). Topographic images were recorded in non-contact mode. The time duration for obtaining one image composed of 256 lines was about 4.27 min at a scanning frequency of 1 Hz. The in-situ optical microscope images were collected using

a digital microscope (KEYENCE, VHX-600E), which achieved a field depth at least 20 times greater than that of traditional optical microscopes. The scanning electron microscope (SEM) and the wavelength dispersive spectrometer (WDS) were executed by the electron probe micro-analyzer (Model JXA-8100, JEOL, Japan).

3. Results and discussion

Fig. 1 shows the topographical changes of 1Cr18Ni9Ti stainless steel in 0.5 M HCl solution over different immersion times. Due to the fatigue effect of the Piezo scanner, these continuous in-situ AFM images shift slightly. To reduce the influence of the shift, part of an image, measuring 10 μm × 10 μm within the 20 μm × 20 μm real time images, is presented to show the same area of the sample. From Fig. 1(a) and (b), rapid dissolution can be observed in the first 15 min immersion. Because this topographical change is reversible when the sample is removed from the solution and exposed to air, it is attributed to the dissolution of air-formed oxide film. The chemical dissolution of oxide film occurred evenly over the whole surface. As a result, polishing scratches became clearer in Fig. 1(b). The dissolution of the oxide film also led to a direct exposure of the metallic substrate on the aggressive medium. Five minutes later, as shown in Fig. 1(c), some defects or inclusions appeared on the surface. Consequently, localized dissolution and micro pitting were initiated, as marked by the black arrow in Fig. 1(c). Between 20 min and 2 h, few changes in the pitting hole can be observed.

In Fig. 2, the profiles of the pitting site at different immersion times are plotted. The position of each profile on the surface is the same, and is marked by the green line in Fig. 1(f). It can be clearly observed that the pitting was initiated after 15 min of immersion. Its depth and size increased rapidly, as shown in Fig. 2(d); then it kept stable as the immersion continued (Fig. 2(e and f)). This region can be characterized as a metastable pitting nucleus in its early stage. The metastable pitting nucleus forms quickly after a uniform dissolution of the oxide film on stainless steel in a reductive acid of dilute HCl solution. This is because the corrosion susceptible sites are directly exposed to the aggressive medium. However, not all metastable pitting can develop into a macro pitting. Many complicated influences are closely related to this process, including repassivation, the nature of surface defects, dissolution of inclusion, and the local environment at the metastable pitting sites [25]. As can be observed in Fig. 1, during the whole immersion period, some corrosion active inclusions eventually dissolved and disappeared, and some chemically stable particles remained unchanged on the surface. SEM and EDS experiments confirmed that these were TiN particles.

Since the 0.5 M HCl solution is also aggressive to the scanner of AFM instrument, in-situ AFM measurement cannot last in it for a very long time. The optical microscope was used to observe in-situ topographical changes in the corrosion process for longer periods. Fig. 3 shows in-situ digital optical microscope images of 1Cr18Ni9Ti stainless steel over the different immersion times in the 0.5 M HCl solution. Fig. 3(a) shows the image of the sample before immersion. It is evident that, except for a couple of cubic TiN particles, the sur-

Table 2Time scale of crystal d_1 – d_8 .

Crystal	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Time scale(s)	0.5–1	1–2	2–4	4–8	8–16	16–32	32–64	64–128

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