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Analysis of corrosion behavior of LY12 in sodium chloride solution with wavelet transform technique①

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[Abstract] Wavelet transforms(WT) are proposed as an alternative tool to overcome the limitations of fast Fourier transforms (FFT) in the analysis of electrochemical noise(EN) data. The most relevant feature of this method of analysis is its capability of decomposing electrochemical noise records into different sets of wavelet coefficients(distinct type of events), which contains information about the time scale characteristic of the associated corrosion event. In this context, the potential noise fluctuations during the free corrosion of commercial aluminum alloy LY12 in sodium chloride solution was recorded and analyzed with wavelet transform technique. The typical results show that the EN signal is composed of distinct type of events, which can be classified according to their scales, i. e. their time constants. Meanwhile, the energy distribution plot(EDP) can be used as "fingerprints" of EN signals and can be very useful for analyzing EN data in the future.

[Key words] electrochemical noise; wavelet analysis; fourier transforms; corrosion; aluminum alloy 2024-T3
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1 INTRODUCTION

The study of spontaneous current or potential fluctuations, which has been designated as electrochemical noise(EN), for the characterization of corrosion processes has received considerable attention in recent years since 1968[1~4]. The study of such fluctuations for the characterization of a corroding interface has an important advantage over all the other electrochemical techniques since it is completely non-perturbative[4~7]. So far, the study of corrosion potential fluctuations was applied, for example, to monitor the onset of events characterizing pitting or stress corrosion cracking corrosion[8~12].

EN data analysis may be performed in the time domain by investigating the shape, the size and distribution in time of the E or I transients observed during certain corrosion processes[10, 13]. Generally, the amplitude of the fluctuation of EN can be correlated with the intensity of the corrosion process, while the fluctuation shape with the type of the process[14]. On the other hand, EN data analysis may be performed using the statistical, the spectral(in frequency domain) and the chaos theory-based methods[7~11, 15].

Recently, a new mathematical tool, i. e. wavelet analysis, for data processing has been developed, which has been proven to be an effective alternative of the above methods[16~21]. And it has received considerable attention in international fields of science and technology, such as signal processing, image processing, phoneme analysis, pattern recognition, quantum physics, and some nonlinear subjects. Meanwhile, It has been used to pick out and further evaluate the fine characteristics of surface structure.

The aim of this work is to investigate the features of free corrosion process of commercial aluminum alloy LY12 in sodium chloride solution, and show that wavelet analysis method can be a valuable option to EN signals.

2 EXPERIMENTAL

Rod specimens of 28.26 mm in diameter and 20 mm in length were cut from commercial alloy. The composition was(mass fraction, %): 4.24Cu, 1.26Mg, 0.65Mn, 0.15Fe, 0.06Si, 0.08Zn, 0.031Ti, less than 0.01Cr, and balance Al. The specimens were connected respectively to a copper wire using screw at one end to accommodate the specimen and provide electrical contact, then mounted in epoxy with the other end exposed. Before testing, the exposed surface was polished using abrasive papers through 500~ 1200 grade, then rinsed in distilled water, decreased in acetone and ethanol and then dried in air.

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EN was monitored as a function of time between working electrode and a saturated calomel electrode(SCE)(reference) using a 1287SI electrochemical interface controlled by CorrWare. This equipment allows resolutions of 1 μV for voltage signals and 1 pA for current signals. EN records, containing 2048 data points, were collected at 2.15 points per second. These conditions define a frequency window in which most usual corrosion processes can be detected. A specific data analysis routine was developed by authors to perform FWT on the EN records.

Test was carried out in solution (1.5 dm^3, 2.0%NaCl, mass fraction) prepared using analytical reagents and deionized water at ambient temperature. During the above experiments, the specimens were removed and examined with optical microscopy to observe the differences in corrosion morphologies.

3 RESULTS AND DISCUSSION

3.1 Wavelet analysis bases

In the orthogonal wavelet series approximation, the time signal sets $S_n(t)(n=1, 2, \cdots, N)$ is transformed into amplitude coefficients of each basis function $S_{J,k}$, $D_{J,k}$, $\cdots$, $D_{1,k}$ (Fig. 1). Thus, the time signal $S(t)$ can be reconstructed by adding together the contributing wavelets weighed by their corresponding coefficients:

$$S(t) \approx \sum_k S_{J,k}\phi_{J,k}(t) + \sum_k D_{J,k}\varphi_{J,k}(t) + \sum_k D_{J-1,k}\varphi_{J-1,k}(t) + \Lambda + \sum_k D_{1,k}\varphi_{1,k}(t) \quad (1)$$

$$S_{J,k} = \int S(t)\phi^*_{J,k}(t)\mathrm{d}t \quad (2)$$

$$D_{j,k} = \int S(t)\varphi^*_{j,k'}(t)\mathrm{d}t \quad (3)$$

where $\varphi^*_{J,k}$ and $\varphi^*_{j,k}$ are the complex conjugate of the basis functions $\phi_{J,k}$ and $\varphi_{j,k}$ respectively, J is often a small natural number which depends mainly on ϕ, φ and N, $j=1, 2, \cdots, J$, $k=1, 2, \cdots, N/2^j$. $\phi_{J,k}$ and $\varphi_{j,k}$ are generated from a pair of functions(the father wavelets ϕ and the mother wavelets φ) through scaling and translation as:

$$\phi_{J,k}(t)=2^{-J/2}\phi(2^{-J}t-k) = 2^{-J/2}\phi(t-2^Jk)/2^J \quad (3)$$

$$\varphi_{j,k}(t)=2^{-j/2}\varphi(2^{-j}t-k') = 2^{-j/2}\varphi\left(\frac{t-2^jk}{2^j}\right) \quad (4)$$

where 2^j acts as scale factor and 2^jk as translation parameter.

Therefore, the wavelet coefficient measures the correlation or the agreement between the wavelet(with its peaks and troughs) and the corresponding segment of the signal. By compressing and expanding the wavelets, the signal can be studied at different resolutions and scales.

3.2 Wavelet analytic results

Fig. 2 shows the FWT analytic results of the free potential fluctuation signal of commercial aluminum alloy LY12 corroding in sodium chloride solution($J=8$). The original signal is plotted in the left top row. The wavelet coefficients are plotted in the remaining rows, going from the fine scale (D_1 coefficients, in the second row) to the coarse scale coefficients (D_8 and S_8). The values of the coefficients are plotted from zero and at approximately the position of the corresponding basis function $\phi_{J,k}$ and $\varphi_{j,k}$. Because the values of the original signal and S_8 coefficients have a much larger dynamic range than the detail coefficients (D_1 to D_8), they are plotted on different vertical scales. Furthermore, since FWT iterations cause a loss of resolution, the 2048 points in the original signal are reduced to 1024 D_1 coefficients, 512 D_2 coefficients, and so on. The number of coefficients resulting from every FWT iteration is inversely related to the width of the basis function that is used in the iteration. Thus, each crystal is related to the features of the signal of a particular scale. The scale range can be computed roughly by Eqn. 5.

$$(C_1^j, C_2^j)=(2^j\Delta t,\ 2^{j-1}\Delta t) \quad (5)$$

where Δt is the sampling interval and j stands for the corresponding crystal(each of the sets of coefficients D_1, D_2, $\cdots$, D_J and S_J is called a crystal).

Fig. 2 also shows that the electrochemical noise signal is composed of distinct type of events, which can be classified according to their scales, i.e. their time constants. Events with characteristically small time constants are taken into account by the fine scale coefficients, $D_1 \sim D_4$. It can be seen that the higher values of this scale coefficients are localized at the position of the narrow spikes of the original signal. The information dealing with large time constant events are included in the $D_5 \sim D_8$

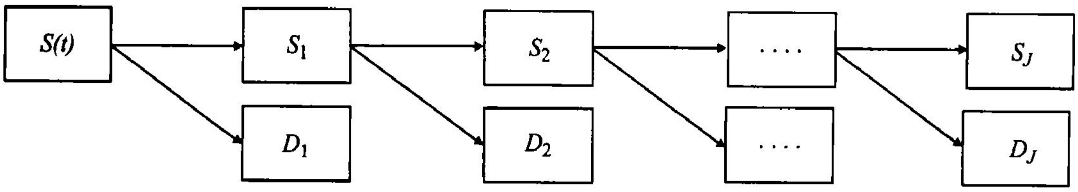

Fig. 1 General scheme of fast wavelet(FWT) analysis algorithm

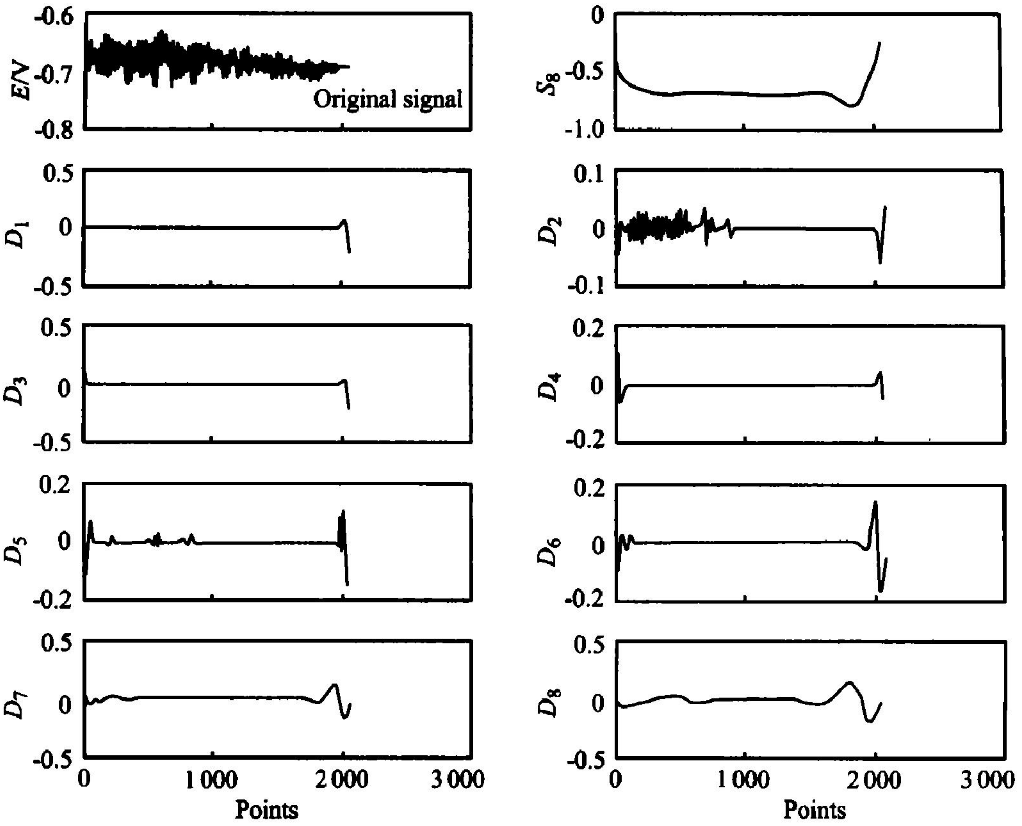

Fig. 2 Wavelets crystals resulting from FWT analysis of EN generated by LY12 corroding in 2.0% NaCl solution(pH7.01)

coefficients. Finally the slowest processes contributing to the original signal would be represented by the S_8 coefficients. Therefore, this kind of plot allows the signal to be viewed over the full time range and considering different scales. Meanwhile, the larger dynamic range of the crystals from D_1 to D_8 and S_8 may be caused by fringe effect.

As can also be observed in Fig. 2 that all transient has some contributions to the original signal, while the event with the largest time constant(S_8) has the dominated contribution. The above results indicate that the original signal is composed of the distinct events with different time constant, but the event with the largest time constant (general corrosion) dominate the whole corrosion process.

Another way of representing the results of wavelet transform is to estimate the contribution of each crystal to the overall signal. Generally, the energy of the signal is calculated using Eqn. (6):

$$E = \sum_{n=1}^{N} S_n^2 \quad (n = 1, 2, \cdots, N) \tag{6}$$

Then, the fraction of energy associated with each crystal can be calculated as

$$E_j^D = \frac{1}{E}\sum_{k=1}^{N/2^j} D_{j,k}^2 \quad (j = 1, 2, \cdots, J) \tag{7}$$

$$E_j^S = \frac{1}{E}\sum_{k=1}^{N/2^j} S_{j,k}^2 \quad (j = 1, 2, \cdots, J) \tag{8}$$

Since the chosen wavelets are orthogonal, the following equation is satisfied:

$$E = E_J^S + \sum_{j=1}^{J} E_j^D \tag{9}$$

The plots of the relative energy accumulated by each crystal vs the crystal name are referred to as the energy distribution plot(EDP). Fig. 3 shows the EDP corresponding to the signal in Fig. 2.

From Fig. 3 can it be seen that there is an increase of the energy with the scale that is more significant starting from the D_8 crystal. The high value for the relative energy of S_8 crystal reflects the fact that the transients with a large scale prevail over those with a small scale in the original signal. According to the earlier studies[22], the material in

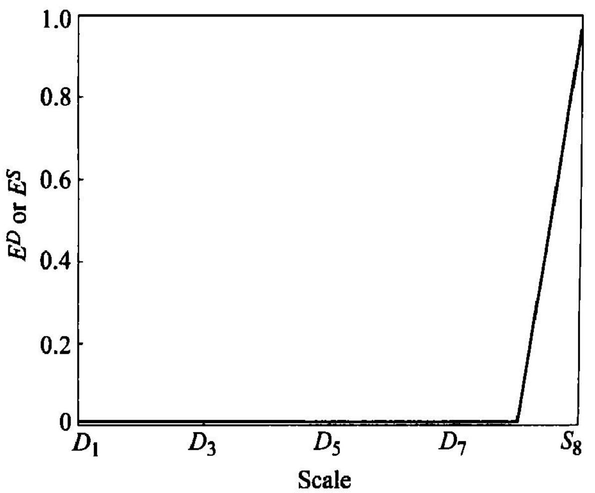

Fig. 3 Energy distribution plots(EDP) corresponding to potential noise in Fig. 2

this experiment may undergo general corrosion, which can also be verified using metallurgical microscope that the surface of the material is covered with a layer of corrosion products.

4 CONCLUSIONS

1) Electrochemical noise signal is composed of distinct type of events, which can be classified according to their time constants. Meanwhile, the EDP can be used as fingerprints of EN signal and can be used to differentiate the corrosion type.

2) During general corrosion of aluminum alloy 2024-T3 in sodium chloride solution, all transients contribute to the original signal, while the event with largest time constant (S_8) has the dominated contribution. Which indicates that those associated with general corrosion are continuous.

3) EN characterized by almost the same small amplitude fluctuation corresponds to that the maximum relative energy is defined at the end of crystal series, while EN with intensive transient peaks(with shorter time constant) out of a smooth background signal corresponds to that the maximum relative energy is defined at the position between well fine coefficients and well coarse coefficients.

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