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Determination of corrosion types from electrochemical noise by phase space reconstruction theory

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ABSTRACT

Chaos theory and the use of phase space reconstruction produce a novel methodology to study electrochemical noise (EN) signals, obtaining novel information to distinguish corrosion types. To evaluate the chaotic nature of electrochemical noise, phase space is reconstructed and the embedding parameter is obtained by the mutual information and Cao's methods. Subsequently, the correlation dimension is calculated. From the correlation dimension, we can conclude that local corrosion shows a higher correlation dimension while passivation shows a lower correlation dimension.

1. Introduction

304 stainless steel (SS) and 316L SS are important metallic materials due to their wide application in the field of engineering [1,2]. The corrosion behaviors of them have been studied using different techniques such as X-ray photoelectron spectroscopy (XPS), scanning Kelvin probe (SKP), dynamic electrochemical impedance spectroscopy (DEIS), scanning electron microscope (SEM), and acoustic emission (AE) [2–7].

Electrochemical noise (EN) is a general term given to fluctuations in the potential and current generated spontaneously by corrosion processes. EN occurs naturally in the electrolyte/electrode interface due to the random ion movements and also originates from the occurrence of cooperative phenomena such as nucleation of pits etc. More deeply, electrochemical noise is associated with all degrees of freedom of the system. It indicates a change in the thermodynamic and kinetic states of the interface and it is the only electrochemical technique that does not disturb the system [8]. The corrosion and corrosion-related processes and mechanisms identified as sources of EN include, among others, the nucleation and propagation of stress corrosion cracks; hydrogen bubble nucleation, growth, and detachment; passive film formation and growth; nucleation, growth, and propagation of pits; abrasion; resistance change and diffusion in solution; high-temperature corrosion; and microbial corrosion and uniform corrosion [9–12]. In general, analysis of the spontaneous fluctuations of potential is beneficial for understanding different corrosion processes [11].

As we know, electrochemical noises usually show complicated behaviors. To describe such complicated behaviors in time series data, to analyze nature, and to predict behavior, frequency analysis such as Fast Fourier Transform (FFT) has conventionally been used. However, frequency analysis is not always effective in estimating such complicated nonperiodic phenomena, because frequency analysis is based on a linear predictive theory and characterizes time series data as a linear superposition of sine waves, with waveforms of various frequencies. Therefore, there is a limit to this analytical procedure with nonlinear phenomena [13,14].

Chaos analysis of the signal is carried out to determine the characteristics of corrosion phenomenon recently [8,15]. Chaos theory and the use of phase space reconstruction have produced a novel methodology to study EN signals, with novel information about the corrosion processes, offering another appropriate explanation for them. Applications of the phase space reconstruction and the theory behind have lately been strongly focused on by medical scientists, physicists, mathematicians and engineers [16]. The most popular application has been in the analysis of time series. Chaos analysis, such as the embedding theorem, the mutual information method, Cao's method, the largest Lyapunov exponent and so on are powerful non-linear methods which enable the extraction of characteristic parameters. The phase space is reconstructed according to the delay coordinate method proposed by Takens [17] and Packard [18]. Here, we define a discrete time array $x(i)$, $i=1, 2, . . . ,n$ obtained by measurement, reconstruct the m-dimension state vector X_n by the delay coordinate method as follows:

$$X_n = x(n), x(n+\tau), x(n+2\tau), ..., x(n+(d_m-1)\tau),$$

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where τ is a time delay and d_m is an embedding dimension. τ and d_m are two important parameters in the phase space reconstruction. Values of τ and d_m are obtained by the mutual information method [19] and Cao's method [20], respectively.

To estimate the attractor dimension, we use the correlation dimension *D*. The most commonly employed method is the algorithm of Grassberger and Procaccia. According to this method, *D* is calculated from the scaling of the correlation function $C_2(r)$ as follows:

$$C_2(r) \approx \lim_{N\to\infty} \frac{1}{N(N-1)} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \Theta\left(R-\left|x_i-x_j\right|\right) \approx r^D, .$$

where Θ is the Heaviside step function, *N* is the number of point in the vector time series, and x_i and x_j are two points of the set. The summation counts the number of pairs of points in the attractor of which the distance $x_i - x_j$ is less than *r*. *D* is calculated from the above equation, to the limit

$$D = \lim_{r\to 0} \frac{\log|C(r)|}{\log(r)}$$

The advantage of chaos approach to signal characterization is that it is diffeomorphically equivalent to the original time series. Moreover, recent analysis of phase space reconstruction has revealed that the correlation dimension is one of the most relevant parameters to describe the signal characteristic [21]. Correlation dimension becomes convenient for characterization of different nonlinear signals, such as heartbeat rate signals, wear signals, snoring sounds, and neuronal spikes. EN signal can be represented by its phase space reconstruction, and a correlation dimension can be assigned. This value is a powerful non-linear method, which enables the extraction of characteristic parameter [10]. It offers tools that bridge the gap between experimentally observed irregular behavior and deterministic chaos theory.

The main objective of the present paper is to determine the corrosion types of 304 SS and 316L SS in different solutions by using EN and chaos analysis. Phase space analysis of the time series obtained from electrochemical potential noise (EPN) is carried out. The possibility of using correlation dimension *D* as a characteristic parameter of corrosion types is described. A study on this topic will significantly enhance the knowledge of extracting characteristic parameters from EN data.

2. Experimental part

The materials that we used were 304 SS (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) and 316L SS (chemical composition, in mass fraction, %: C ≤0.030%; Cr 17.0%–21.0%; Ni 9.00%–13.0%; Mo 2%–3%; Mn ≤1.5%; Si ≤1.5%; P ≤0.045%; S ≤0.04%; Fe, balance), which were supplied by Taiyuan Steel Company, China. A three-electrode configuration was used for the experiments. Two nominally identical electrodes were immersed in the selected solutions. The surface of the working electrodes was abraded with silicon carbide paper (from 400# to 2000#), with an exposed area of 1 cm^2. Two of 304 SS or 316L SS were made as the working electrodes

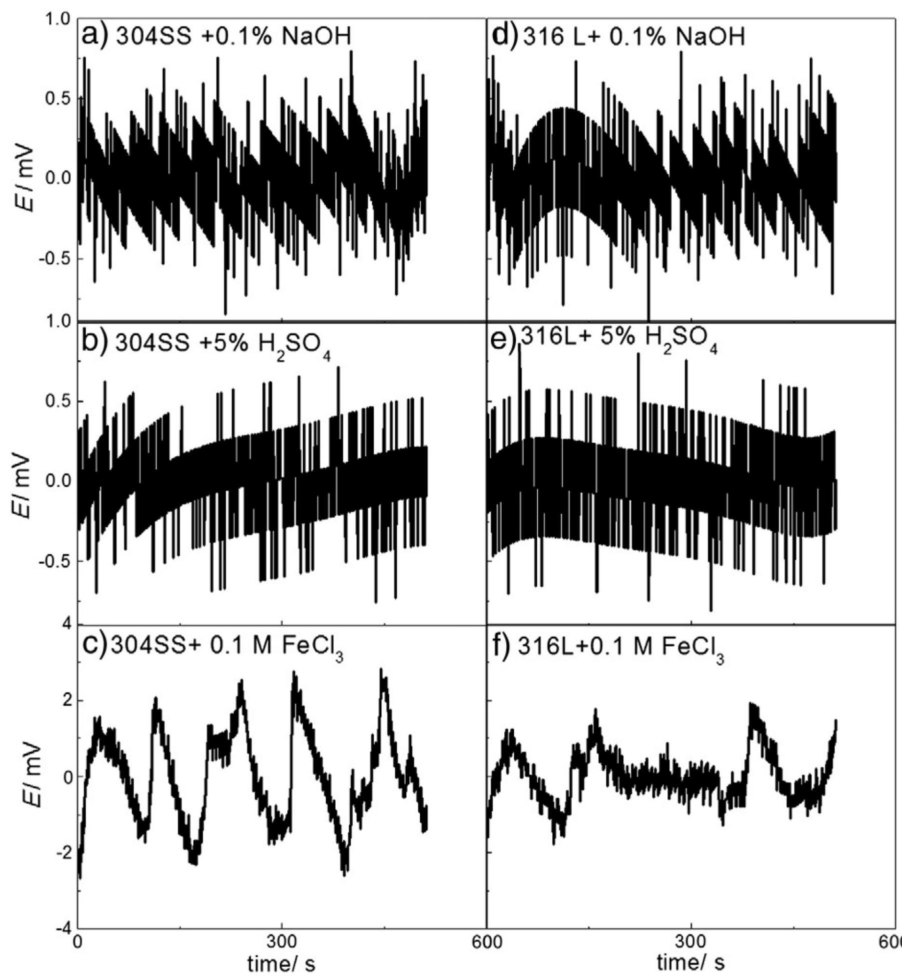

Fig. 1. EPN of 304 SS and 316L SS after immersion in 0.1% NaOH, 5% H_2SO_4, and 0.1 mol/L $FeCl_3$ for 1 h (after a dc was removed).