The Significance of Correlation Dimension Obtained from Electrochemical Noise

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ABSTRACT

The corrosion types of Q235 carbon steel and nuclear grade 304 stainless steel (304 NG SS) in different solutions are investigated by electrochemical noise (EN) technique. EN data are analyzed by using phase space reconstruction theory. With the obtained correlation dimension from the phase space reconstruction, the chaotic behavior of EN is quantitatively evaluated. It is concluded that local corrosion shows a higher correlation dimension while passivation shows a lower correlation dimension. We propose that the correlation dimension increases with the complexity and uncertainty of the signals from passivation to local corrosion, which is the physical meaning of correlation dimension for EN.

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1. Introduction

Many semimacroscopic phenomena related to corrosion, either localized or uniform, are stochastic by nature.¹ There are various electrochemical methods to study the corrosion phenomena, including electrochemical impedance spectroscopy (EIS),^{2–4} electrochemical noise (EN),⁵ polarization curve,^{6,7} and so on. EN appears as a choice for its study, with a number of attractive features for corrosion research and engineering. EN measurement has been proved to be one of the most promising methods for detecting corrosion types, such as passivation,⁸ uniform corrosion,⁸ local corrosion,^{7,9} and stress corrosion cracking.^{10–12}

Though EN measurement is an in-situ electrochemical method, how can the EN data be efficiently analyzed and reliably interpreted is one of the most concerned issues. In our previous paper,¹³ we proposed to analyze electrochemical potential noise (EPN) by phase space reconstruction theory or chaos theory—a kind of nonlinear mathematics. In order 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. We conclude that local corrosion shows a higher correlation dimension while passivation shows a lower correlation dimension. However, why local corrosion present a higher correlation dimension is still not clear.

In this paper, we select another two typical steels, Q235 carbon steel and nuclear grade 304 stainless steel (304 NG SS) as the research subjects. Q235 carbon steel is a type of important metallic material due to its wide application in the field of architectural and engineering structures. 304 NG SS, one of the dominated materials in the primary circuit, is widely used in the nuclear power plants. Therefore, a study on the corrosion behavior of Q235 carbon steel and 304 NG SS has noted significance. The first objective of the present paper is to determine the corrosion types of Q235 and 304NG SS in different solutions by using electrochemical noise and chaos analysis. Correlation dimension, performing as a characteristic

parameter of corrosion types is described. The second objective of the present paper is to discuss the physical meaning of correlation dimension for EN: why local corrosion presents a higher correlation dimension while passivation shows a lower correlation dimension?

2. Experimental

2.1 Material

Q235 carbon steel and 304NG SS plates were provided by Taiyuan Iron and Steel Company. The chemical composition can be seen from Table 1. The steel plate was made into the specimen (10 mm in length, 10 mm in width, and 2 mm in thickness) by a Wire Cutter Electrical Discharge Machine. Specimens were connected to a copper wire at one end to provide electrical contact, and then embedded in epoxy resin. The surface of the specimen was abraded with silicon carbide paper (from 400# to 2000#), and then they were ready for the operation after having been washed by distilled water, degreased by ethanol and dried by cool air.

2.2 EN measurement

In situ EN measurement, a three-electrode configuration was introduced for the experiments. Two nominally identical electrodes were immersed in the selected solutions. The working electrodes were polished till 2000-grit emery and the area exposed to solution was 1 cm². Two identical Q235 carbon steels or 304NG SS were made as the working electrodes and the reference electrode was a saturated calomel electrode (SCE) with a salt bridge. The EPN was measured between one of the working electrodes and the reference electrode through a zero resistance ammeter (ZRA) mode on a VersaSTAT 4 electrochemical workstation (Princeton Applied Research, USA) and VersaStudio control software at about room temperature (25 ± 3°C). The sampling frequency was 2 Hz. The sequences of solutions used, together with the corrosion behavior observed, are summarized in Table 2. Table 2 reflects the corrosion types of Q235 carbon steel and 304NG SS in different solutions, which have been reported by other researchers.⁸

Table 1. Chemical composition of Q235 carbon steel and 304NG SS (wt%, Fe-balance).

Elements	C	Si	Mn	P	S	Cr	Ni	N	Cu	Co	B
Q235	0.230	0.107	0.460	0.020	0.032						
304NG SS			≤			18.50–	9.00–		≤		
	0.035	1.00	2.00	0.030	0.015	20.00	10.00	0.080	1.00	0.06	0.0018

Table 2. Solutions and corrosion types.

Material	Solution	Corrosion types
Q235 carbon steel	0.1% NaOH (wt%)	Passivation
	5% H ₂ SO ₄ (wt%)	uniform corrosion
	0.2 mol/L NaCl	local corrosion
304NG SS	0.1% NaOH (wt%)	Passivation
	5% H ₂ SO ₄ (wt%)	uniform corrosion
	0.1 mol/L FeCl ₃	local corrosion

2.3 Chaos analysis

Matlab software was used to reconstruct phase space and estimate the correlation dimension of the EPN. This data was then plotted in log-log format and the slope was determined using a linear squares regression technique. From this slope, correlation dimension was determined.

2.4 Microstructure characterization

The surface microstructure was characterized using a metallographic microscope (Olympus Optical Microscope BX51M).

3. Results and Discussion

3.1 Electrochemical potential noise

Figure 1 shows three kinds of EPN data for passivation, uniform corrosion and pitting of Q235 carbon steel, being immersed in 0.1% NaOH, 5% H₂SO₄, and 0.2 mol/L NaCl solution for 30 min and 6 h, respectively. The direct current (dc) component was first removed from the original EN data by a 5-order polynomial fitting. EPN data represent typical changes of electrochemical signals during the corrosion process. The EPN for Q235 carbon steel after immersion in 0.1% NaOH for 30 min and 6 h are shown in Figs. 1(a) and 1(b), respectively. The signals are similar to white noise, showing very high repetition rates of potential fluctuations within amplitudes of 0.75 mV. Figures 1(c) and 1(d) show the EPN after immersion in 5% H₂SO₄ for 30 min and 6 h, respectively. These signals are also like white noise, and the amplitudes of potential fluctuations are about

Figure 1. EPN of Q235 carbon steel after immersion in 0.1% NaOH, 5% H₂SO₄, and 0.2 mol/L NaCl for 30 min and 6 h (after a dc was removed).

Figure 2. EPN of 304NG SS after immersion in 0.1% NaOH, 5% H₂SO₄, and 0.1 mol/L FeCl₃ for 30 min and 6 h (after a dc was removed).

Figure 3. (Color online) Phase space reconstruction of the EPN signals in Fig. 1, corresponding to passivation (a, b), uniform corrosion (c, d), and local corrosion (e, f).

0.7 mV. Figures 1(e) and 1(f) give EPN after immersion in 0.2 mol/L NaCl solution for 30 min and 6 h, respectively. Compared with passivation and uniform corrosion, EPN signals of pitting show some transient peaks with amplitudes of 1 mV.

The EPN of 304NG SS in 0.1% NaOH, 5% H₂SO₄, and 0.1 mol/L FeCl₃ solution for 30 min and 6 h are presented in Figs. 2(a)–2(f), respectively. Similar EN characteristics can be seen for 304NG SS. Likewise, EPN of passivation and uniform

corrosion are similar to white noise, showing very high repetition rates of potential fluctuations within amplitudes of 0.75 mV. But as for local corrosion, it presents some transient peaks with amplitudes of 4 mV.

3.2 Reconstruction of phase space

The attractors of the reconstructed phase space for Fig. 1 and Fig. 2 are shown in Fig. 3 and Fig. 4, respectively. We can see that

Figure 4. (Color online) Phase space reconstruction of the EPN signals in Fig. 2, corresponding to passivation (a, b), uniform corrosion (c, d), and local corrosion (e, f).

Figure 5. (Color online) Calculated correlation dimensions of the attractors in Fig. 3 and Fig. 4.

the three-dimensional phase space trajectories are all strange attractors with different shapes, so the results confirm that these signals are chaotic.

From Figs. 3 and 4, we find that the attractors present a structure of “spherical shape” for passivation and uniform corrosion [Figs. 3(a)–3(d) and 4(a)–4(d)], but they present a structure of “ellipsoidal shape” for local corrosion [Figs. 3(e), 3(f) and 4(e), 4(f)].

3.3 Calculation of correlation dimension

Figures 5(a)–5(f) show typical results when the correlation dimension curves are estimated. A linear region is found in the $\ln C(r)$ – $\ln(r)$ plots, so the EPN data have fractal properties, and the slope of $\ln C(r)/\ln(r)$ is the correlation dimension. The correlation dimensions of passivation for Q235 carbon steel are 1.3812 and 1.3795, and the correlation dimensions of uniform corrosion are 1.5122, 1.5394 while the correlation dimensions of local corrosion

are 2.1296 and 2.0311. Similar D values can be observed for 304NG SS. Therefore, the obtained correlation dimension can distinguish the differences among the signals that generated during corrosion process. In summary, the highest correlation dimensions can be found in local corrosion while the lowest in passivation. The fluctuations of EPN signal are related to the electrode reaction rate, so various corrosion types show distinctive EPN characteristics, indicating that the electrode reaction rate are different.

In order to observe the variation of correlation dimension D as a function of immersion time, EN data up to 6 h are processed to calculate D values, as shown in Figs. 6(a) and 6(b). It was found that D remains basically unchanged during the 6 h immersion, which can be possibly explained by the fact that the corrosion rate is basically invariable during an immersion time of 6 h. In a 6-hour immersion test, the D value of pitting presents a more positive value, denoting that pitting process shows a higher electrochemical activity.

3.4 Morphology analysis

In order to observe the typical morphology analysis of Q235 carbon steel and 304NG SS after the EPN experiments directly, morphology is characterized by an optical microscope, shown in Fig. 7. No corrosion occurs on the electrode surface for passivation process [Figs. 7(a), 7(d)]. A general corrosion occurs on the surface of the two steels in 5% H_2SO_4 solution [Figs. 7(b), 7(e)], and many well-developed corrosion pits are formed on the electrode surface in 0.2 mol/L NaCl solution and in 0.1 mol/L $FeCl_3$ solution [Figs. 7(c), 7(f)]. Comparing Fig. 7(c) with Fig. 7(f), we have found that the pit size of Q235 carbon steel is larger than that of

Figure 6. (Color online) Variation curves of correlation dimensions of Q235 carbon steel (a) and 304NG SS (b) as a function of immersion time.

Figure 7. Morphology of Q235 carbon steel in 0.1% NaOH (a), 5% H_2SO_4 (b), and 0.2 mol/L NaCl (c); morphology of 304NG SS in 0.1% NaOH (d), 5% H_2SO_4 (e), and 0.1 mol/L $FeCl_3$ (f) after the EPN measurement.

304NG SS, indicating that a more serious corrosion occurred on Q235 carbon steel. Similar difference can be seen in Fig. 7(b) and Fig. 7(e), revealing that Q235 carbon steel shows a more serious corrosion in 5% H₂SO₄ solution.

3.5 A physical meaning of correlation dimension

Any physical quantity should have a physical meaning, and a physical meaning of correlation dimension for EN is proposed according to some reference. In recent years, chaos analysis is widely used in data analysis of electroencephalogram (EEG), respiratory movement, heart rate variability (HRV), and internal carotid artery (ICA).^{14–16} In our previous paper,¹³ we provide a new methodology to study EN signals, obtaining new information to distinguish corrosion types based on phase space reconstruction. We selected 304 and 316L stainless steel as this thesis's subjects, and studied the relationship between the EN signals and corrosion types of the two steel. We discovered that local corrosion showed a higher correlation dimension while passivation showed a lower correlation dimension. Therefore, the increased D may be associated with the increased complexity of the signals. For passivation process, the EN source is simpler there than in the uniform corrosion and local corrosion. Also, electrodes of uniform corrosion and local corrosion are more active than passivation. For uniform corrosion, the electrochemical process is mainly anodic dissolution and hydrogen bubble nucleation, growth, and detachment. The EPN signal of local corrosion has higher complexity and uncertainty due to the nucleation, growth, and propagation of pits, which would lead to a higher correlation dimension. From Figs. 1 and 2, we can see that the EPN signals of passivation and uniform corrosion resemble “white noise”, but the EPN signals of local corrosion have many transient peaks. Therefore, the EPN signals of local corrosion have higher complexity and uncertainty. The correlation dimension of EPN is associated with the irregularity and complexity of the electrochemical process which is not totally random but deterministic random.

4. Conclusions

This work demonstrates the significance of correlation dimension obtained from electrochemical noise. We select Q235 carbon steel and 304 NG SS as the research subjects. EN data is analyzed by using phase space reconstruction theory. With the obtained

correlation dimension from the phase space reconstruction, the chaotic behavior of electrochemical noise is quantitatively evaluated. It is concluded that local corrosion shows a higher correlation dimension while passivation shows a lower correlation dimension. It is proposed that the increased correlation dimension is associated with the increased complexity and uncertainty of the signals from passivation to local corrosion, which is the physical meaning of correlation dimension for EN.

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References

1. D. H. Xia, S. Z. Song, J. H. Wang, and H. C. Bi, *CIESC J.*, **63**, 1797 (2012).
2. S. Amami, C. Lemaitre, A. Laksimi, and S. Benmedakhene, *Corros. Sci.*, **52**, 1705 (2010).
3. D. H. Xia, S. Z. Song, J. H. Wang, H. C. Bi, and Z. W. Han, *Trans. Tianjin Univ.*, **18**, 15 (2012).
4. D. H. Xia, S. Z. Song, J. H. Wang, H. C. Bi, and Z. W. Han, *Acta Phys.-Chim. Sin.*, **28**, 121 (2012).
5. A. M. Lafront, F. Safizadeh, E. Ghali, and G. Houlachi, *Electrochim. Acta*, **55**, 2505 (2010).
6. H. D. Jung and A. Alfantazi, *Electrochim. Acta*, **51**, 1806 (2006).
7. D. H. Xia, S. Z. Song, J. H. Wang, H. C. Bi, and Z. W. Han, *Trans. Nonferrous Met. Soc. China*, **22**, 717 (2012).
8. S. Girija, U. Mudali, V. Raju, R. Dayal, H. Khatak, and B. Raj, *Mater. Sci. Eng., A*, **407**, 188 (2005).
9. Y. Z. Lu, S. Z. Song, and L. H. Yin, *Trans. Nonferrous Met. Soc. China*, **15**, 619 (2005).
10. R. Zhao, Z. Zhang, J. B. Shi, L. Tao, and S. Z. Song, *J. Cent. South Univ. Technol.*, **17**, 13 (2010).
11. G. Du, W. K. Wang, S. Z. Song, and S. J. Jin, *Anti-Corros. Methods Mater.*, **57**, 126 (2010).
12. G. Du, J. Li, W. K. Wang, C. Jiang, and S. Z. Song, *Corros. Sci.*, **53**, 2918 (2011).
13. D. H. Xia, S. Z. Song, J. H. Wang, J. B. Shi, H. C. Bi, and Z. M. Gao, *Electrochem. Commun.*, **15**, 88 (2012).
14. N. Burioka, G. Cornelissen, F. Halberg, and D. T. Kaplan, *Clin. Neurophysiol.*, **112**, 1147 (2001).
15. R. Carvajal, N. Wessel, M. Vallverdu, P. Caminal, and A. Voss, *Comput. Methods Programs Biomed.*, **78**, 133 (2005).
16. D. Yilmaz and N. F. Guler, *Digit. Signal Process.*, **20**, 401 (2010).