Analysis of current transients of AISI 1020 steel corrosion in sea water using electrochemical noise methods and optical monitoring.

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Introduction

Among the different types of corrosion, localized corrosion is common in seawater and is the most difficult process to control. However, with the use of appropriate electrochemical and optical techniques is possible to estimate and to identify the processes that occur in the corrosive environment. Electrochemical noise, EN, can be defined as random fluctuations of the current or potential observed in electrochemical systems [1]. Noise measurements are valuable information sources about complex electrochemical reactions in non-equilibrium corrosion systems. In EN technique the experiments can be performed under open circuit conditions, E_{oc}, using two symmetric working electrodes, WE_1 and WE_2, between which the measured current noise signal, I_n, and a reference electrode, RE, to permit monitoring of the potential noise V_n. To analyze the results obtained different mathematical methods to deconvoluted the data can be used such as Fourier [2] and Wavelet Transform [3]. This last one is generally interpreted using energy diagrams in which, considering specifically corrosion data, can differentiate among the corrosion types. The electrochemical noise signal profile is related to the corrosion type and mechanisms, therefore is possible to analyze the steel corrosion in seawater samples and evaluating the corrosion processes along the time.

In this work were used the EN technique and optical monitoring to identify the main corrosion processes that occur in the AISI 1020 steel in artificial seawater. To interpret the I_n we used the wavelet transform and energy diagrams. It was possible to make qualitative and quantitative analysis of the changes occurring on the type of corrosion during the onset of corrosion of steel.

Experimental

As working electrodes AISI 1020 steel rods were used. Two identical samples, WE_1 and WE_2, with A = 0.5 mm^2 were embedded in polyester resin side by side separated by 1 cm, and polished using 0.25 µm diamond paste. The electrodes were cleaned with acetone in ultrasound bath. A saturated Ag/AgCl RE was used to measure the electrochemical data: potential noise and current noise were collected simultaneously. The artificial seawater was prepared in agreement to recommendation of Lyman and Fleming [4]. Figure 1 shows the schematic diagram of the electrochemical cell in an optical microscope, so that it was possible to record changes in the WE_1 surface during the acquisition of electrochemical noise signals.

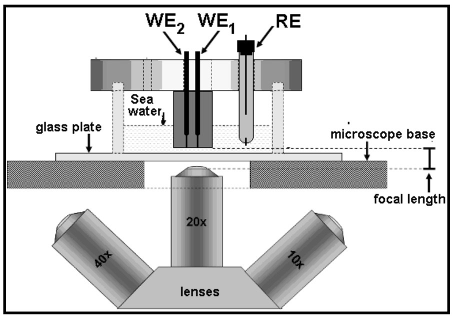


Figure 1: Schematic diagram to record corrosion while the EN measurement.

To perform the EN measurements at E_{oc} it was used an Autolab-PGSTAT30 with ECN module controlled by NOVA 1.6 software. Noise was registered at a sampling frequency of f_s = 6 Hz. The signal analysis was performed using the Matlab® Wavelet Toolbox 4.4 software and the Daubechies-wavelets “db4” orthogonal function was applied in eight levels of decomposition. The main property of the chosen function is that energy of the analyzed signal is equal to the sum of energies of all components obtained by wavelet transform and because they look like fractal-like signals and therefore faster convergence of wavelets coefficients is expected. In this work the interpretation of results was performed by estimating the energy contribution of each level of decomposition in relation to the original signal. This type of analysis is well described in papers by Abale et al [3].

Results and Discussion

After immersion in the solution, V_n and I_n have intensity in the order of 10^{-4} V and 10^{-8} A, respectively. Different works in the literature [5, 6] have been proposed that intensity noise is related with pit formation. In this case, abrupt changes in the potential and/or current are related to the local destruction of the passive layer which are followed by the repassivation. Then, I_n decrease to low values again. Therefore, large current transients are related to the nucleation, growth and pit repassivation or another type of localized corrosion. On the other hand, potential transients are related to the capacitance of the metal/solution interface [6].
Figure 2 shows the signals for AISI 1020 steel electrode in sea water during three different times: immediately after immersion (Fig 2A), 5 hours (Fig. 2B) and 14 hours (Fig. 2C) after immersion.

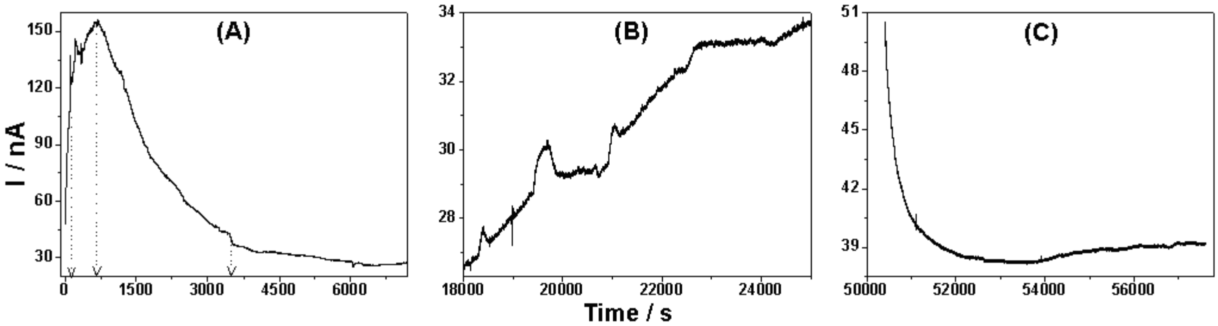
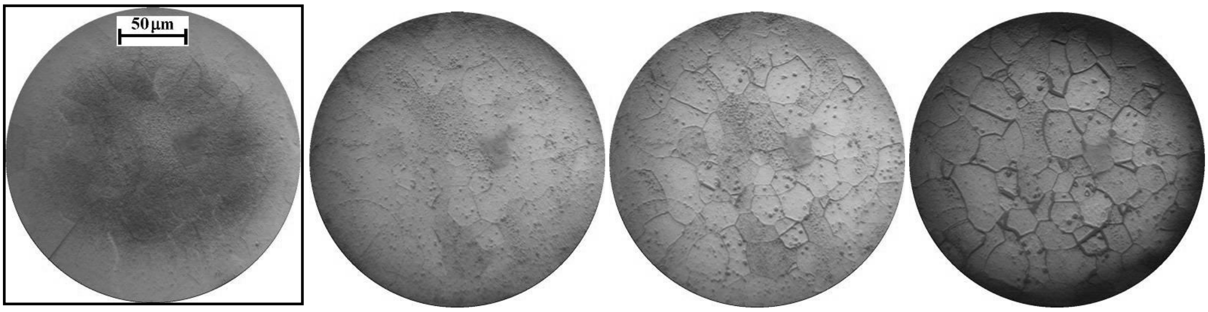


Figure 2: Electrochemical noise current signals to the AISI 1020 steel in sea water.

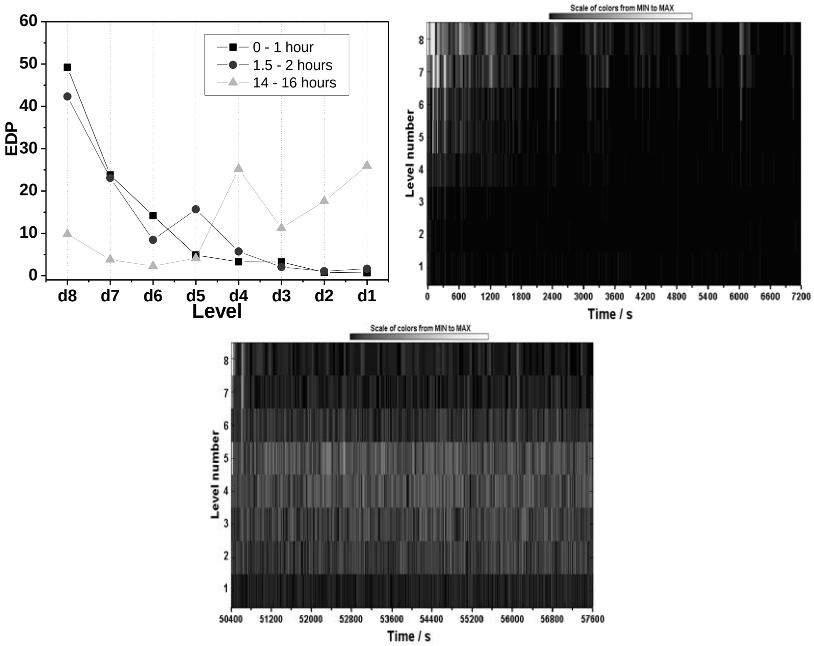
In an initial stage, up to 665 s, it is possible to observe oscillations in the current signal, which may be related to the initiation of located attack in regions more susceptible to corrosion such as inclusions. The micrograph recorded at this time, Figure 3, shows the beginning of these processes that occur up to approximately 3.470 s. After 1 hour, can be seen in the micrographs mainly attacks in the intergranular regions with a slight increase in the corrosion of grain (general corrosion) after 12 hours.



t = 665 seconds **t = 3,470 seconds** **t = 2 hours** **t = 12 hours**

Figure 3: Optical micrographs of the WE_1 surface obtained during acquisition of EN data.

In the current noise signal, changes in these processes are not readily apparent, however, can be evidenced after analysis using the wavelet transform. Figure 4A shows an energy diagram plot (EDP). In EDP it is clear that during the first hour there is a predominance of intergranular and pitting corrosion by the energy accumulated relative d_5-d_8 levels characteristic of this type of corrosion [3]. From 1.5 hours, it is possible to observe that the energy contribution of localized processes begin to decline indicating a change in the type of corrosion. This corroborates with the end of punctual attack in the inclusions. After 14 hours it is observed that the general corrosion becomes predominant, as evidenced by the increase in cumulative energy d_1-d_4 levels. In Fig. 4B and 4C the two-dimensional time (serial number of sampling point) − frequency (level, scale) representation is shown. Each rectangle on the plane shows the corresponding wavelet coefficient in gray-scale code with black representing the minimum value and white representing the maximum value. In this type of representation, the transform discrete, we can see sudden changes in signal evidenced by the transient current at the time of formation of pitting or other localized processes such as lighter regions in the diagram. In Figure 4B these processes appear especially in the early high intensity 600 s. Figure 4C shows a constant distribution of the etching process generally from 14 hours as may be seen by the lighter regions between the levels d_2-d_5.



(A) **(B)** **(C)**

Figure 4: A) EDP corresponding to the EC signals in the Fig. 2; B and C) the two-dimensional visual presentation of discrete wavelet transforms of signals.

Conclusions

Through the use of electrochemical noise technique and wavelet analysis it was possible to characterize the initial processes of AISI 1020 steel corrosion in seawater. There was a considerable change in the type of corrosion during the first hour of immersion of the steel. Initially (to ~ 2 hours) corrosion processes are predominantly localized by means formation of pitting and intergranular corrosion. After approximately 14 hours of immersion, there was a dominance of general corrosion processes. The interpretation of signals by wavelets was confirmed by optical micrographs, and therefore can be valuable to this type of study, making it clear that some types of processes are often not identified by other techniques.

Acknowledgements

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References

1. J.L. Dawson, Electrochemical Noise Measurement for Corrosion Applications, ASTM STP 1277, 1999.
2. Y.F. Cheng, J.L. Luo, M. Wilmott, Electrochimica Acta, 45 (2000) 1763-1771.
3. A. Aballe, M. Bethencourt, F. Botana, M. Marcos, Electrochimica Acta, 44 (1999) 4805–4816.
4. J. Lyman, R.H. Fleming, Journal of Marine Research, 3 (1940) 134.
5. L. Organ, J.R. Scully, A.S. Mikhailov, J.L. Hudson, Electrochimica Acta, 51 (2005) 225–241.
6. Y. Cheng, M. Wilmott, J. Luo, Applied Surface Science, 152 (1999) 161–168.