

A Preliminary Analysis of Correlation between Electrochemical Noise in Digital Signals and Images in Corrosion Studies of 316 SS.

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Abstract

The phenomenon of corrosion in metallic materials such as 316 stainless steel (316SS), produce a degradation which is mainly represented by the lost of metallic properties. One way to study this phenomenon is analyzing microscope digital images of materials exposed to corrosive processes, and the analysis of electrochemical signals using electrochemical noise measurements. The traditional technique used to study the electrochemical noise provides a limited resolution, and it is almost impossible to perform further processing such as spectral analysis by traditional Fourier methods. Therefore, DSP oriented analysis tools were applied to the 1-D electrochemical signals and 2-D microscope images looking further features extraction and the results are presented in this paper.

1. Introduction

This paper shows the research work about the analysis of microscope digital images of metals affected by corrosion. Using image processing techniques, patterns are extracted, and correlation is searched with electrochemical signals obtained from the same corrosion process. Under controlled experimental conditions and an exposure time of 3 hr., the 316 SS undergo some pitting. This cause appearance change in the acquired microscope image with furthers pitting corrosion when with the exposure time is increased. We believe that an important relationship exist between the images and

the electrochemical signals obtained from the same process.

1.1. Preliminary studies

The scanning electron microscope let us to obtain digital images with special characteristics. One of them is the direct relationship between image gray level and material depth. Each color level in the acquired image represents a profundity level. This process of image acquisition is called secondary electrons projection. Each returned electron has a different energy level, i.e., if the electron goes across far way, then it will return with less energy charge.

Our first studies about digital image analysis to extract information about corrosion levels, were carried out with a Ni-40Cr and Fe-40Cr alloys exposed 150 hr at 1200° C in pure O₂ [1]. Figure 1 shows the morphology of the Ni-40Cr alloy together with two transversal scan lines and its representation as profiles in digital signals. The second signal shows the depth level of the black pit respect to the neighboring profundity levels. The amplitude is greater than in other sections of the signal. Figure 2 shows the results for the Fe-40Cr alloy. Here, the obtained corrosion patterns were very different than those for the former alloy. The Fe-40Cr alloy has signals with higher amplitude and frequency components than those recorded for the Ni-40Cr alloy.

Observing only the microscope images, it is very difficult to extract and separate more advanced corrosion features. The application of the FFT showed that the geometry of the

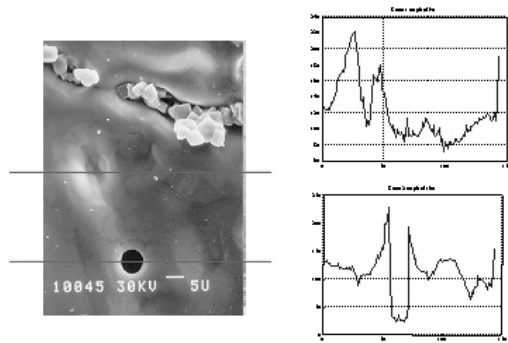


Figure 1. NiCr alloy with high temperature corrosion, and two transversal cuts.

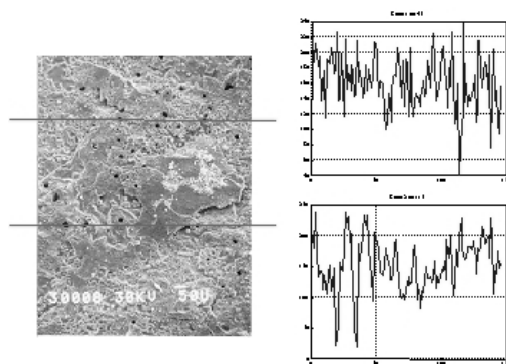


Figure 2. FeCr alloy with high temperature corrosion, and two transversal cuts.

pit was wider for low frequencies, and the high frequencies are related to the narrow pits. Thus, our interest was focused on the low frequencies, because it is understood that a microscope image shows so much information, and the most important information about corrosion is hidden by the high frequencies.

The NiCr and FeCr low pass filtered images and histograms in figure 3, shows that the image for the Ni-40Cr alloy (above left) has much more important corrosion evolution features compared with the Fe-40Cr alloy (above right). Also, the histogram for the Ni-40Cr alloy (bottom left) has a more relevant set of gray levels (representing greater corrosion) than that obtained for the Fe-40Cr alloy (bottom right).

To conclude a final result, a thresholding masks were applied, obtaining two new binary images. The next expressions were used

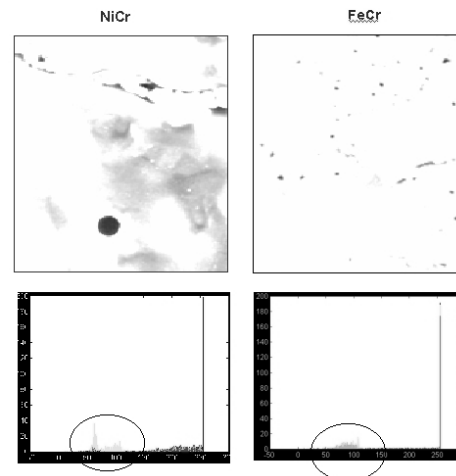


Figure 3. Results obtained after filtering, and their histograms.

if

$$g(x, y) > Threshold \Rightarrow f(x, y) = T_{max}$$

and

$$g(x, y) \leq Threshold \Rightarrow f(x, y) = T_{min}$$

where $g(x,y)$ is the original image, $Threshold$ is a determined level gray, and T_{max} and T_{min} are the maximum and minimum gray level scale values.

After the filtered images were converted to binary images, edge detection was done to detect the most advanced corrosion damage. Figure 4, shows the images for the Ni-40Cr alloy. The images and information obtained along the experiment permitted us to obtain the next values, deterioration of 23.83%, with $893.62 \mu^2/hr$ as the corrosion rate, which is an area equivalent to 0.158%/hr. For the Fe-40Cr alloy it was found a 6.52% of deteriorated area, and a corrosion rate of approximately $244.5 \mu^2/hr$, which is an area equivalent to 0.043 %/hr.

This analysis is valid for both Ni-40Cr and Fe-40Cr alloys because both of them were exposed at the same environmental conditions.

2. Electrochemical Noise

Electrochemical noise is a general term to describe the random fluctuations in current or potential that occurs in electrochemical processes. The theoretical treatment of the

phenomenon is still incomplete, but there are many useful applications based on both scientific studies and corrosion monitoring applications.

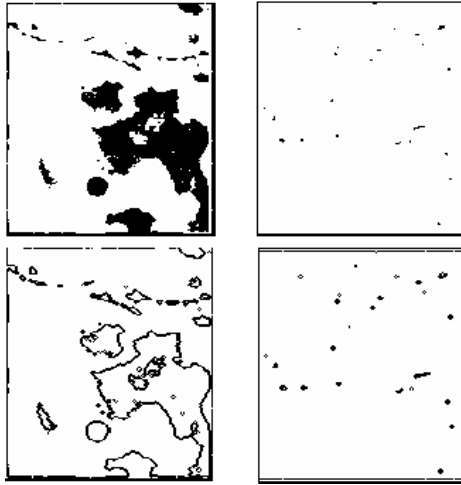


Figure 4. These images permitted us to compute the velocity of deterioration on the material surfaces.

The measurement method does not include any external perturbation to the corroding system. Therefore, it can be applied to real structures. The instrumentation required to perform the measurements is reasonably simple; particularly with digital signal processors, and data acquisition techniques. The localized corrosion processes, sometimes difficult to monitor with other techniques tend to generate strong electrochemical noise signals [2].

The starting point to develop a theory of electrochemical noise is the theoretical analysis of the noise associated with a randomly occurring, brief pulse of charge, related to the occurrence of each event being independent of any other event. This is known as a Poisson process, and the simplest example is the flow of electronic current, in which, each event is the passage of an individual electron through the measuring circuit. Assuming the noise current, I_n , as the instantaneous current minus the mean current, it can be shown that the noise current is given by

$$\overline{I_{2n}} = 2elb \quad (4)$$

where

$\overline{I_{2n}}$ is the mean squared noise current

e is the charge on the electron
 l is the average current flowing
 b is the bandwidth of measurement

3. Sources of noise

The major sources of noise observed in electrochemistry and corrosion can be ascribed to macroscopic random (stochastic) phenomena. They include partial faradaic currents, adsorption/desorption processes, surface coverage, and, in the case of localized corrosion, the initiation of pits and mechanical effects resulting from film disruption and passivation processes.

In this case, the source of noise developed in the electrochemical process is the pitting initiation process. This process often results in metastable pit nucleation and propagation, giving rise to current transients lasting for a time of the order of 1 second, and involving a charge of the order of 10^{-6} C (corresponding to around 10^{12} atoms). Thus, the noise associated with pitting corrosion is much larger than that observed for general corrosion [2].

In general, there are two different ways to measure electrochemical noise:

- The potential noise of a single sample can be monitored relative to a low noise reference electrode.
- The current noise between a pair of identical electrodes can be measured. A similar measurement can also be made on a single electrode by controlling its potential relative to a low-noise reference electrode.

It is also possible to combine both of these techniques by measuring the current noise between two identical electrodes while concurrently monitoring the potential noise of the coupled electrodes relative to a low-noise reference electrode or to a third identical electrode. This technique offers interesting possibilities in the analysis of the resultant data, and probably is the best measurement technique for corrosion monitoring

Most of the electrochemically-generated noise occurs at relatively low frequencies (1 Hz or less), and the measurement procedure

requires deals with very small amplitude signals.

As a preliminary investigation of the nature of the electrochemical noise from a specific system, the simplest method is to record the current or potential with an X-t recorder. However, this method provides a limited resolution, and it is virtually impossible to perform further processing such as spectral analysis. Hence, for more sophisticated work the time of recording should be processed using mathematical techniques [2].

In general, it is accepted that electrochemical noise contains useful information about electrochemical processes, but there is not consensus about which is the best approach to extract such information. To some extent, this is because the best method varies according to the type of processes being studied. This is an area where further development is required.

Electrochemical noise belongs to the general category of random low-frequency processes. These stochastic processes are described either by probability density function equations or in statistical terms [3].

4. Laboratory tests

Laboratory tests were carried out using a pitting cell (see figure 5). The metal of study 316 SS, was placed into the cell and exposed to the environment. In this case water with 5% of NaCl, at 30°C for 3 hr.

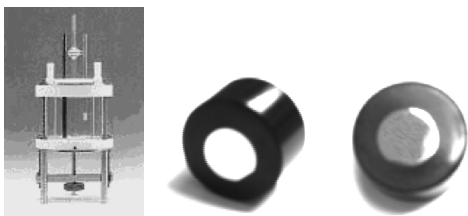


Figure 5. Pitting Cell (right), and probates of stainless steel 316

After the preparation of specimens, some SEM photos of specimens in the polished-only condition were taken as a reference to compare later with the new photos after the exposure to the environment.

Applying the electrochemical noise measurement technique, we acquired two types of noise signals, which are the

potential-time record (mV) and the current-time record (mA), see figure 6.

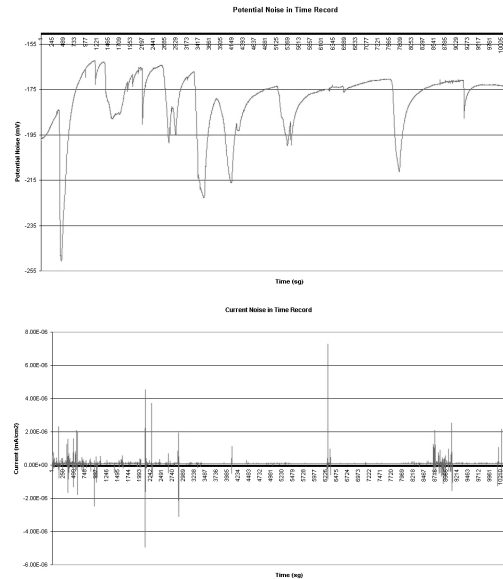


Figure 6. Potential noise measurement (above) and Current noise measurement (below) vs time (3 hrs).

The above potential and current signals were sampled at 1Hz during 3 hrs (10800 samples). The potentials levels were between -155 mV and -255 mV and the current fluctuations between -0.005 mA and $.007$ mA. The analysis of both signals shows that a potential drop initiates a corrosion pitting process, meaning that some localized corrosion is occurring over the metallic surface (film breakdown). When the potential noise moves to a more positive value, then the opposite effect occur i.e. a repassivation process.

Figure 7 shows the first 112 samples of the potential signal. With this higher resolution to evaluate the corrosive behavior we can see a signal with a determined slope, and noise (high frequencies). The amount of slope may be a signature for the different metal alloys.

The electrochemical noise measurement data can converted to corrosion rates by calculating the noise resistance (R_n), and inserting its value into the Stern-Geary equation instead the resistance (R_p) [4]. The R_n was calculated according to the following equation:

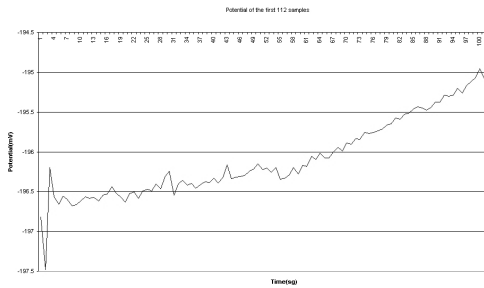


Figure 7. The first 112 samples of the potential signal.

$$R_n = \left(\frac{\sigma V}{\sigma I} \right) \quad (5)$$

where

σV Standard deviation of the potential noise

σI Standard deviation of the current noise

5. Future work for electrochemical noise analysis and DSP.

Often, a particular spectral component occurring at some specific instant can be of particular interest. In such cases, it may be beneficial to know how the time intervals in these particular spectral components occur. Wavelet transform is capable of provide the time and frequency information simultaneously, giving a time-frequency representation of the signal. The time-domain signal is filtrated with several high pass and low pass filters (filterbank), which filters out either high frequency or low frequency portions of the signal. This procedure is repeated and some portion of the signal corresponding to some frequencies being removed from the signal [5].

Our interest is to apply and find results by using the wavelet transform due to electrochemical noise and transversal scans in digital images representing non-stationary signals. In this applications is important to know what frequency is related to what time and its amplitude.

6. Conclusions

The main proposes of this work is to find some patterns of the corrosion behavior for 316 SS at the conditions before mentioned. The frequency and time domain of electrochemical noise potential and current

let us to compare some statistical characteristics found in electrochemical noise analysis. Also, it is possible to obtain a relationship with the transversal scans in the microscope images, where this type of signal shows different geometric forms based on high and low frequencies. Figure 10, shows some kind of extracted patterns.

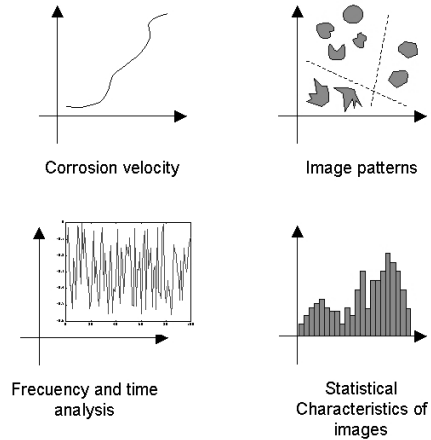


Figure 7. Pattern extraction between electrochemical signals and digital images

The power spectrum and its slope are related with the corrosion rate. Also, we have found some relationship of statistical characteristics in images where the method of corrosion measurement between electrochemical signals (typically in units of distance over time) and images (μ^2 / hr).

An attempt has been done in trying to find corrosion behavior patterns and a correlation between electrochemical signals, corrosion rate, power spectrum, slopes, statistical characteristics in digital images and multi resolution analysis (wavelet).

With the successful extraction of these kind of patterns, we could understand better the corrosion behavior of 316 SS during the immersion in a water and NaCl solution, and also to predict corrosion rates for this and other alloys.

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