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Copper patina corrosion evaluation by means of fractal geometry using electrochemical noise (EN) and image analysis

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A B S T R A C T
Chaos theory and the use of fractal geometry originated a new methodology to study EN signals obtaining new information on corrosion processes. A clear direct relationship is obtained between fractal analysis of EN time series and images.

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1. Introduction
Copper is one of the most important metallic materials due to its wide application in the field of engineering [1–4]. The protective properties of copper patina and the magnitude of its protection have been studied using different techniques such as XPS, IRAS, XRD, and SEM/EDS [5–9].

Electrochemical noise (EN) is the only electrochemical technique that does not disturb the system. Electrolyte film is very small and any disturbance can affect it; which is the case with atmospheric corrosion. Current EN measurement is now frequently applied following the corrosion process [10].

Some reports [11,12] carry out a fractal analysis of the signal to determine the characteristics of corrosion phenomenon. Chaos theory and the use of fractal geometry have produced a new methodology to study EN signals, with new information about corrosion processes, allowing us to have a better explanation for them [13,14].

Theory and application of the Hurst exponent [15] have lately been strongly focused on by physicists, mathematicians, and engineers. The most popular application has been in time series analysis. The Hurst definition is very linked to the concept of fractal geometry, defined as \( D_f = D_e - H \) (\( D_f \) is the fractal dimension of the object under observation). For a time series, \( D_f \) lies between 1 and 2 and for an image between 2 and 3. \( D_e \) is the Euclidean dimension corresponding to the object to which fractal dimension will be determined. In case of a time series, the value will be 2, and in case of an image, the corresponding value will be 3.

Hurst exponent values range between 0 and 1. The value of 0.5 refers to a complete random behaviour. Under these circumstances, there is no correlation between the present and the future element. When the Hurst component value lies in the interval \( 0.5 < H < 1 \), this indicates persistence of the phenomenon or, in other words, autocorrelation. The interval \( 0 < H < 0.5 \) indicates anti-persistence, or negative autocorrelation. Based on these concepts, Reman [16] proposed the Predictability index on time series (\( I_{ps} \)) which is defined by the following equation:

\[
I_{ps} = 2 \abs{D_f} - 1.5
\]

\( D_f \) is the fractal dimension of the time series. Considering that the Hurst exponent has also been associated with roughness, another Surface Predictability index (\( I_{pi} \)), could be defined according to the following equation:

\[
I_{pi} = 2 \abs{D_i} - 2.5
\]

\( D_i \) is the fractal dimension of the image.

Image characterization using fractal dimension based on micrographics is a very robust methodology; the texture of surface micro-structural changes is independent of different variables like illumination [17]. The advantage of fractal approach to surface characterization, is that it is insensitive to the structural details, and the structure is characterized by single descriptor, the fractal dimension \( D \) [18]. Moreover, recent statistical comparison of relevant roughness parameters revealed that the fractal dimension is the most relevant parameter to describe the surface topography [19]. Fractal dimension becomes convenient for...
Fig. 1. Time series and Hurst estimation.

\[ Y = (3.94 \times 10^{-8}) \times 0.42 \]

\[ Y = (5.19 \times 10^{-8}) \times 0.367 \]

\[ Y = (7.7 \times 10^{-8}) \times 0.517 \]
characterization of different topographies, such as those obtained by electrochemical processes of controlled anodic dissolution, commonly used for shaping and surface structuring of metals [20].

Nowadays, quantitative results are obtained using digital analysis of the signals [21]. Corrosion phenomena created surfaces of very complex appearance, very difficult to describe and to understand. Time series and fractals can be used as a tool to help us interpret and understand these surfaces. Some authors have found relevant information about corrosion phenomena [22] using this procedure. Current EN signal contains information concerning the activity of the electrode surface. An equivalent surface can be generated based on time series of similar fractal characteristics [23].

The main objective of the present paper is to determine the protection capacity of copper patinas formed in an exposure at different atmospheres using electrochemical noise (EN) and image analysis. Fractal analysis of the time series obtained by current EN and images is also carried out. A comparison is made in order to find out if a relationship between both types of fractal analysis can be made.

2. Experimental part

Experimental procedure carried out for atmospheric exposure of copper samples is described in a previous paper [24]. Corrosion of copper was evaluated in five sites, named as P2, P4, P5, P7 and P8.

EN signal can be represented by its geometry and a fractal dimension can be assigned. This value has been very important when characterizing corrosion phenomena. Roughness–length method was used to determine Hurst (H) and the corresponding fractal dimension for every time series. In the roughness–length relationship method, the standard deviation, or root-mean-square (RMS) roughness of the data, is taken in windows.

Fig. 2. Image and texture of copper patina.
of size $w$, rather than the vertical range. For a self-affine trace, the RMS roughness $S(w)$, (where $s =$ standard deviation), measured in a window of size $w$, is related to the Hurst exponent as $[25,26]$: 

$$S(w) = cW^H$$

Plotting $\log W$ versus $\log S(W)$ you will find that the slope is the Hurst coefficient, related to the fractal dimension of the time series ($D_f$) by the following expression $[15]$: 

$$D_f = 2 - H$$

Digital images were obtained using an optical reflection microscope OLYMPUS PMG3. The digital camera of the microscope was coupled to a personal computer. Images (512 X 480 pixels) were captured on grey tone; four images for each sample. Fractal dimension was calculated for each image (values obtained were very similar) and the data closest to the average value was selected.

In order to estimate the fractal dimension of the images, a 2-D FFT transformation was carried out on the digitalized image. The results were then fed to a forward 2-D FFT utility and the mean spectral energy density as a function of the wave number was measured. This data was then plotted in log-log format and the slope was determined using a linear squares regression technique. From this slope, fractal dimension was determined. IMPACT Pro V5.11 software $[27]$ was used. Fractal dimension of an image and the Hurst coefficient were linked by the following equation: 

$$D_f = 3 - H$$

3. Results and discussion

Three time series set for points P2, P4 and P7 are presented in Fig. 1. There are also linear fit to obtain Hurst coefficient and estimate fractal dimension using roughness–length technique. The morphology of the time series is very similar, but there is a significant difference in amplitude, which follows the order P4, P5, P2, P8 and P7. The lower value corresponds to P4 and the higher value corresponds to P7. It is an indication, as it has been proposed, that with a higher standard deviation, a more intense corrosion rate is obtained $[28,29]$. This means that for higher amplitude of the signal, a lower protective patina is obtained because the faradaic processes of corrosion phenomena are more intense. It is in complete agreement with the Faraday laws and with the material loss that occurred.

Digital images of the patinas on grey tone are presented in Fig. 2. In Fig. 1, a representation of the texture (considering local changes in pixel brightness) is made: texture of an image is an important parameter in the use of pattern recognition to characterize basic constituents of a material in a surface.

Corrosion processes produce a texture corresponding to the rough structure of the surface. These surfaces are an indication of the different intensities of the corrosion processes that will occur. It is very important to have a quantitative evaluation of the visual appearance of the textures of the objects that are under analysis. Taking this into consideration, texture analysis can be carried out based on brightness characteristics. Texture implies working in a three dimensional space, while x and y correspond to the position of the pixel, and z, the intensity of the brightness.

An image is a value matrix presented in a discrete way to assign a value. In this case, it is an 8 bit image on grey tone corresponding to integer values from 0 to 255, generating a matrix of $512 \times 480$ positions. A statistical analysis of the image under fractal characteristic is possible.

A clear relationship is shown between the EN current time series fractal parameters and the fractal analysis of patina images formed in the different atmospheres (Fig. 3). This is an indication of the robustness of the methodology. It is very well known that micro cells formed on the surface are the cause of the corrosion phenomenon and its distribution determines the morphology of the attack.

![Fig. 3. Fractal parameters relationship.](image-url)
EN signal is the result of the interaction of micro cells, related to its position and intensity. In this particular case, EN measurement was carried out when there was already a copper patina formed, yet not in the initial period. Under these circumstances, microcells should exist in the copper surface covered by a layer of corrosion products containing soluble anions and cations. These components dissolve in the water that is added. This situation makes it possible to generate equivalent surfaces based on EN information and vice versa, generating EN information based on equivalent surfaces.

Digitalized images on grey tone and texture corresponding to the different formed patinas are presented in Fig. 2. Through visual observation, it is not easy to characterize the surface. However, an inverse relation is noted through the calculation of the fractal dimension (as can be observed in Fig. 3A). A correlation coefficient value $R = -0.93$ and standard deviation (SD) 0.05 is obtained. This means that by using fractal geometry, a relation is obtained between the protective characteristics of the formed patina through image analysis and through the signal of EN. Hurst coefficient time series value versus fractal dimension of the surface is plotted in Fig. 3B. An excellent fitness is obtained ($R = 0.84$, SD = 0.07). According to the Skerry [30] proposal, corrosion protective capacity of the coating improves with lower Hurst coefficient values. When fractal dimension of the image is lower ($D_i$), the roughness of the surface is also lower. For very porous surfaces or with higher $D_i$, a lower protective capacity should be expected and consequently, a more intensive corrosive attack.

IPs versus $I_{pi}$ are plotted in Fig. 3D. A good inverse relation is obtained ($R = -0.94$), showing an interaction between the different active sites that are distributed across the surface and reflected on the EN current signal. This confirms that images and EN signal are a representation of the electrochemical processes on the surface, and also its distribution. On top of that, it confirms that the electrochemical corrosion process can be represented by graphic or numbered data.

4. Conclusions

A clear direct relationship is obtained between fractal analysis of EN time series and images of corroded copper samples. Surfaces can be characterized using EN and/or images because the distribution and intensity of micro cells on the corroded surfaces produce different morphologies.

Digital analysis of images obtained from corroded surfaces is an important tool for diagnosing protective characteristics of patina formed on copper surfaces.

In addition to electrochemical techniques, corrosion processes can be analyzed using image analysis.

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References