Short Communications

Observation of Copper Corrosion Oxide Products Reduction in Metallic Samples by Means of Digital Image Correlation

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The use of digital image correlation for optical monitoring of corrosion processes occurring in a metallic sample is here proposed. The formation and reduction of corrosion products (oxides) over the surface of an old copper coin immersed in an electrolytic basic mixture is analyzed through a standard electrochemical characterization and, simultaneously, registered by means of a simple optical experimental setup which corresponding sequential images are registered, stored and digitally processed utilizing a digital image correlation method. This method may be helpful for controlling electrochemical reduction of corrosion products processes, and could be also applied in antique objects cleaning and restoration.

Keywords: Optical monitoring, corrosion reduction processes, digital image correlation

1. INTRODUCTION

It is well known that economical losses related with metallic structure corrosion have overcome 3% GNP of developed countries (as in USA) and more than a 7% in developing countries like Peru [1]. So, as it can be seen, the necessity of carry on serious studies about corrosion phenomena is quite evident; furthermore disciplines such as Electrochemistry are dedicated to understand several materials behavior under different environment conditions through estimation of specific parameters like corrosion rates or the resistance of materials, and elaboration of theoretical models related with the obtained results.

Corrosion is usually defined as the alteration or degradation of a metal due to its interaction with natural environment. In particular, electrochemical corrosion is characterized by the existence of an anodic zone (where corrosion takes action), a cathodic zone and an electrolyte, being both in direct electrical contact [2]. It is well known that corrosion is defined through electrochemical reactions
which are defined as chemical reactions involving the transfer of electrons, and consequently oxidation and reduction are the main processes involved [3].

Several procedures for measuring related parameters are commonly used; some of these, known as gravimetric techniques, quantify the weight of a sample before and after being subjected to corrosion tests and after this an average rate of the electrochemical process as a function of time are obtained. Other useful tools are the well known potential pH or Pourbaix diagrams, which are calculated and sketched on the basis of the thermodynamics theory of electrochemical processes for each metallic material and give us information about their state accordingly to two parameters: hydrogen ion concentration (pH) and electrode potential(Fig.1) [4, 5]. Three main zones can be identified for these diagrams: a) the immunity zone (metals do not experiment any corrosion process), b) the passivation zone where metals present corrosion and corrosion products are formed, isolating them from environment and providing additional protection, and c) the free dissolution (corrosion) zone without corrosion products formation.

![Pourbaix diagram for copper species.](image)

Electrochemical techniques are another group of procedures based on the Faraday law “the amount of mass involved in an electrochemical process is directly proportional to the amount of electricity circulating through the system”, so that a corrosion process can be monitored by measuring voltage and current values simultaneously. The possibility of electrochemical monitoring allows using of instruments such as voltmeters and ammeters in order of a real-time tracking. Among the most well known electrochemical techniques, potentiodynamic and potentiostatic electrical polarization curves, electrochemical noise or impedance spectroscopy can be mentioned [6-10].

1.1. Electrochemical Principles.

Although corrosion is generally considered as a problem, it is also known its employing as a tool for printed circuit boards fabrication, metallic surfaces finishing (electrochemical polishing) or even for artistic refinement applications in sculptures. Some materials are subjected to electrochemical
processes to generate strong corrosion products, which as it turned out protect the material from environment as in anodized aluminum; recently, an interest on electrochemical techniques for restoration of pieces with alterations due to environmental conditions has emerged [13, 14]. In this case and, accordingly with electrochemical theory, some corrosion products (oxides) can be taken to a metallic state by means of an electrochemical reaction which can be reversed to the one which originated such products. When a metal like copper experiments an oxide process the corresponding chemical reaction is:

\[ \text{Cu} \leftrightarrow \text{Cu}^+ + e^- \]  \hspace{1cm} (1)

\[ \text{Cu} \leftrightarrow \text{Cu}^{2+} + 2e^- \]  \hspace{1cm} (2)

where Cu is the reduced state of copper (metal), Cu\(^+\) and Cu\(^{2+}\) are the oxidation states, and e\(^-\) are electrons loaned by copper [4, 5]. The reactions presented in Eqs. (1) and (2) are reversible, therefore it is possible in principle to reduce the oxidized species.

In corrosion processes this is not entirely accurate, since problems of irreversibility do arise. In the presence of oxygen, and water

\[ \text{Cu} + \text{H}_2\text{O} \leftrightarrow \text{Cu}_2\text{O} + 2\text{OH}^- \]  \hspace{1cm} (3)

\[ \text{Cu}_2\text{O} + \text{O}_2 \leftrightarrow \text{CuO} \]  \hspace{1cm} (4)

being Cu\(_2\)O more stable. With the presence of water, chlorides or sulphates, the following reactions with hydroxide oxide formation, can take place

\[ \text{Cu}_2\text{O} + \text{SO}_4^- + \text{H}_2\text{O} \leftrightarrow \text{CuSO}_4(\text{OH})_n\text{H}_2\text{O} \]  \hspace{1cm} (5)

\[ \text{Cu}_2\text{O} + \text{Cl}^- + \text{H}_2\text{O} \leftrightarrow \text{Cu}_2\text{Cl}(\text{OH})_2 \]  \hspace{1cm} (6)

Recently, the interest into the use of optical techniques for corrosion monitoring has increased. Holographic interferometry was employed for measuring displacements in electrodes electrically polarized immersed in aqueous solutions [13]; Michelson interferometry was used to measure optical phase displacements by monitoring interference fringes shifting which is related with superficial deformations and also with material weight loss [13, 14]. On the other hand, structured light projection has been used to quantify material loss due to corrosion processes [14]. The employment of these techniques allow a qualitative analysis, identifying the type of corrosion (generalized or localized) and also a quantitative one as degradations caused by corrosion can also be accurately measured [14, 15].

1.2. Digital Image Correlation.

Accordingly with digital image processing theory, cross-correlation can be used as a tool to quantify the similarity degree between two images, as defined by:
\[ f(x) \cdot g(x) = \int_{-\infty}^{\infty} f^*(u)g(x + u)du \] (7),

where \( f(x) \) and \( g(x) \) are signals, \( f^*(x) \) is the complex conjugated of signal \( f(x) \) and \( u \) is a fictional variable for integration [16, 17]. By using the Fourier transform properties the cross-correlation can be expressed as the following:

\[ f(x) \cdot g(x) = \mathcal{F}^{-1}(u) \cdot G(u) \] (8).

In order to determine the degree of similarity between two images, it is possible to do the mathematical operation in the Fourier domain by a multiplication, allowing the use of well known algorithms for calculation of a Fast Fourier Transform (FFT); here we use this tool to observe the evolution of oxides grown on the surface of a copper coin on its first stage. As the electrochemical process is carried on the appearance of our coin changes and losses its original form; when the image of the coin obtained at the beginning is compared with a later one where the evident change is originated by corrosion products, we can qualitatively observe the degradation from the original. When the same electrochemical reaction is applied in the reverse way, the usefulness of imaging correlation method can be appreciated as it offers a non-contact way to quantitatively evaluate the moment in which an image quite close to the original have been recovered. The advantage of using such a tool is based on the modesty of the experimental setup and the relative simplicity of the applied algorithms.

2. EXPERIMENTAL SETUP AND DEVELOPMENT

In order to obtain the optical monitoring of the electrochemical processes occurring in a metallic sample, a simple experimental setup was implemented. It consisted of a copper coin fixed into a \( 10 \times 10 \times 8 \text{ cm}^3 \) electrochemical cell where an electrolytic solution prepared by 1 l of distilled water mixed with 26 g NaCl and 3.6 g Na\(_2\)SO\(_4\), was added (Fig. 2). Besides enclosing the sample under investigation (working electrode), the cell also contained a reference electrode and an auxiliary or counter-electrode (calomel and graphite, respectively) immersed in the solution; an ACM Gill 8AC potentiostat is used for controlling and perform electrochemical tests, which consist of cyclic potentiodynamic polarization test that give potential/logarithmic current density plot. The obtained dependence curves allow identification of the regions type and rate of the corrosion processes presented in the sample, as well as corrosion products formed.

Electrochemical experiments were performed using an ACM Instruments potentiostat controlled by a personal computer. Potentiodynamic polarization curve was obtained by varying the applied potential from \(-700 \text{ mV}\), up to \(+350 \text{ mV}\) at 60 mV/s scan rate. Before the experiments, the corrosion potential \( E_{\text{corr}} \) value, was measured during approximately 30 minutes until it was stable. All potentials were measured using a saturated calomel electrode (SCE) as reference electrode. The counter electrode was a platinum wire. All tests were performed at room temperature.
Figure 2. Experimental setup to obtain electrochemical dependences of the sample.

On the other hand, a white-light beam coming from a commercial low-power LED source is focused on the surface of the sample with a $f=200$ mm lens and passed through two equal linear polarizers for output intensity controlling; once it illuminates the sample inside the electrochemical cell, its reflection is collected by using another $f=200$ mm lens to a CCD camera connected to a PC where corresponding images of the coin are stored for their later analysis (Fig. 3).

Figure 3. Optical setup for monitoring of oxidation-reduction corrosion processes.

In the second experimental stage (corrosion products formation) the sample is electrochemically polarized at a fixed $-225$ mV electrochemical potential, delivering it into the passivation region. The potential is fixed during a 3000 seconds time interval as the electrochemical current density is monitored, to determine corrosion and film growth. The images of the coin into the cell corresponding to this particular process are simultaneously recorded, with a 10 seconds interval between each consecutive shot.
Once images are recorded, the cross-correlation operation of the initial image (taken at the beginning of the process) with every subsequent image captured by the imaging system is performed, to obtain the maximum value corresponding to each correlation and to compare these values with the complete electrochemical behavior as observed in the potentiostatic polarization curve.

When all the corrosion products were completely formed at the metallic surface, the third experimental stage was begun (corrosion products reduction).

The sample is now electrochemically polarized to a fixed -550 mV electrochemical potential, and set in the cathodic region, causing the reduction of its corrosion products. The same procedure used above for images recording and processing in the passive region, is repeated under this cathodic reduction condition.

3. RESULTS

Here in this work, electrochemical polarization is used, namely potentiodynamic and potentiostatic polarization curves. The sample is immersed in an electrolyte with known pH and by means of a reference electrode and an auxiliary control electrode, an electrical potential scanning is applied and the current value is simultaneously measured; the obtained data are sketched as follows: the current values are on the “abscises” logarithmic axis and the potential values on the “ordinates” axis.

On Fig. 4 a polarization curve for a copper sample in a pH 8 solution is shown, which also corresponds to the sample utilized in this work (old copper coin).

![Figure 4. Potentiodynamic polarization curve for a copper coin in a 3% NaCl solution.](image)

It can be observed on the graph two regions divided by an equilibrium electrochemical reaction potential $E_{eq}$ ($E_{corr}$) the lower region belongs to the cathodic region where the material is immune, which can be verified in a Pourbaix diagram. The equilibrium potential is the point where the
degradation (or corrosion) process begins, once the equilibrium point is surpassed (here is where the anodic region starts). It can be also adverted a zone inside the cathodic region where despite the voltage increases, the current is kept constant; this is the “passivation zone” which for the present case is located at -250 mV and the trasspassive region at about 250 mV.

At figure 5(a), the electrochemical curve obtained for the first experimental stage, where the electric current is monitored as a function of time for a fixed -225 mV electrochemical potential is shown. The sequence of maxima cross-correlation values calculated for the consecutive images during the same time interval is shown at figure 5(b).

**Figure 5.** First experimental stage (corrosion products formation). a) Potentiostatic curve, and b) Maxima correlation curve for the same time interval.

Accordingly with figure 5(a), the initial maximum current density value is rapidly diminished due to the formation of passivating corrosion products, which at the same time protect the sample once they are formed (after approximately 200 sec). It can be assumed that the quality of an image is related to the reflectance of its surface.

Then in our particular case the cross-correlation value between two consecutive images can also be affected by the optical quality of the metallic surface which is in turn modified by the corrosion process. Because of these considerations, we can easily explain the observed decay of the cross-correlation curve behavior (Figure. 5b), being due to the fast corrosion oxides formation, which degrades the quality of the images obtained, and this is why the evident similarity among figures 5(a), and 5(b). Dependences can be easily understood, and additionally the loss of the initial image quality as the test proceeded was clearly observed during this experiment, partly due to the oxides formation and also to the turbidity increase of the initially clear aqueous electrolyte solution (Figure 6).
Figure 6. Graphic composition of the oxides formation process (during the first 100 seconds of test).

Figure 7(a) illustrates the electrochemical curve obtained during the third experimental stage, as the electrochemical current density is monitored during the same time interval but now at a fixed -550 mV electrochemical reduction cathodic potential value, fixed potentiostatically. At figure 7(b) the sequence of maxima cross-correlation values calculated for the consecutive images during the same time interval are shown.

Figure 7. Corrosion products reduction). a) Potentiostatic curve for the electric current during time interval. b) Maxima correlation curve for the same time interval.

As it can be seen, the highest correlation maximum is observed at 750 seconds after the test started, which is roughly the same time value for the electrochemical current density decreased, reaching its stationary value at -0.130 mA/cm² approximately indicating oxide reduction. This current density value corresponds also to the moment in which the corrosion products reduction reaches its peak value and highest performance. Although the correlation curve was decaying in a similar way as the potentiostatic cathodic current density, it presents a maximum value.
This could possibly be explained in terms of the reduction and/or precipitation of the oxides previously formed (second experiment), and cleaning of the surface of the initial corrosion products formation, as can be seen in figure 8. Images are difficult to be mutually distinguished at first sight.

In any case, what it is clearly highlighted here is the presence of a peak on the cross-correlation curve which might be related to the moment at which the initial image of the non-corroded sample surface, matches with a later image where the sample have reached the best possible recovering of its clean and original surface profile (Figure 9). [18]. This can be take advantageously as a tool for a precise control in the electrochemical reduction process, mainly because it is quite difficult to identify the exact moment in which the test must be stopped, by a direct optical observation of the system (see Figure 8).

Figure 8. Oxides reduction process; a) at the beginning of the process, b) after 900 seconds of the total time interval, c) amplified area of “a)” and, d) amplified area of “b”.

Figure 9. Metal coin with original cleaned surface and profile.
This could be applied successfully during the recovery of historical pieces or works of art from the sea bed, and/or the assessment of the restoration and conservation process of corroded archaeological artifacts [11, 12, 18].

4. CONCLUSIONS

The main contribution of this proposal is the possibility to use digital image cross-correlation as a complementary tool for conventional electrochemical monitoring techniques, for example, in the detection of the moment in which a time-depending recovering test applied on metallic samples must be stopped as required. This in order to avoid an unplanned destruction of the sample by continued application of electrochemical current density. This technique can consequently be of interest in the area such as metallic restoration structures affected by corrosive environments.

REFERENCES


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