Quantification of corrosion products formation onto a copper sample by digital holographic microscopy

Cuantificación de la formación de productos de corrosión sobre una muestra de cobre por microscopía holográfica digital

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ABSTRACT:

In this work an application of digital holographic microscopy as a tool for oxide layer growth monitoring onto a copper sample, as well as determination of corrosion products formation rate and corrosion type taking place (localized corrosion or uniform corrosion) is presented.

Key words: Digital Holography, Holographic Microscopy, Corrosion.

RESUMEN:

En este trabajo se presenta una aplicación de microscopía holográfica digital como una herramienta para el monitoreo del crecimiento de una capa de óxidos sobre una muestra de cobre, así como la determinación de la velocidad de formación de productos de corrosión y el tipo de corrosión (localizada o uniforme) que está llevándose a cabo.

Palabras clave: Holografía Digital, Microscopía Holográfica, Corrosión.

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1. Introduction

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 anodic and cathodic zones in direct electrical contact [1]. It is well known that this corrosion type 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 [2]. It is also well known that economical losses related with metallic structure corrosion have overcome 3% PIB of developed countries (as in USA) and more than a 7% for underdeveloped countries [3]. So, as it can be seen, the necessity to carry on serious studies about corrosion phenomena is quite evident; furthermore disciplines as Electrochemistry are dedicated to understand the physical-chemical behaviour of several materials under different environment conditions, through estimation of specific parameters like corrosion rates or resistance of materials, and elaboration of theoretical models related to obtained results. A special interest on applying optical techniques to investigate corrosion processes have been recently increasing. K. Habib was probably the first in using holographic interferometry principles to get the monitoring of metallic electrodes

immersed into saline solutions [4]. A group of researchers from the CIICAP applied Michelson interferometry to perform optical monitoring of corrosion processes on metallic samples at similar conditions [5]. Some other optical methods like digital in-line holography [6,7], digital speckle pattern interferometry [8], and structured light projection [9] to quantify the effects of corrosion on metallic surfaces have been used. In this work we applied the concepts of digital holographic microscopy (DHM) to perform the monitoring of corrosion products grown on a copper sample. Digital holography is a relatively new technique based on the concepts of optical holography, introduced by Dennis Gabor in 1948 [10], that allows numerically access to information of not only the amplitude but also the phase related to the object wave field. In digital holography, the holographic interference pattern is optically generated by superposition of object and reference beams, which is digitally sampled by a CCD camera and transferred to a computer as a numbers array, avoiding the needing of chemical developing as used in conventional holography. Figure 1 shows the basic scheme for digital holographic recording.

According with wave-interference theory, the intensity value captured by the CCD sensor is:

$$I_h(x, y) = I_R(x, y) + I_O(x, y) + \\ + E_R(x, y)E_O^*(x, y) + E_R^*(x, y)E_O(x, y), \quad (1)$$

Fig. 1. Numerical recording of holograms.

where $I_h(x, y)$ represents the resultant intensity distribution at the hologram plane, or CCD plane (optical hologram), $I_R(x, y)$ and $I_O(x, y)$ represent the reference and the object intensity distributions respectively; the other two terms represent the object wave front multiplied by the conjugated reference beam, and the conjugated object wave front multiplied by the reference beam. According with diffraction theory, numerical reconstruction is done by multiplying Eq. (1) by the original reference wave:

$$h(x, y) = E_R(x, y)[I_R(x, y) + I_O(x, y)] + I_R^2(x, y)E_O(x, y) + E_R^2(x, y)E_O^*(x, y). \quad (2)$$

The first line of Eq. (2) is the reference wave, multiplied by a factor. It represents the non-diffracted wave passing through the hologram (zero-order diffraction). The second term (second line in Eq. (2)) is the reconstructed object wave, forming the virtual image; the real factor $I_R^2(x, y)$ only influences the brightness of the image. The third term (third line in Eq. (2)) generates a distorted real image of the object. The reason for the distortion of the real image is the spatially varying complex factor $E_R^2(x, y)$, which modulates the conjugate object wave $E_O^*(x, y)$ image formation. The discrete digital hologram captured by the CCD is obtained from the optical hologram as following:

$$I_h(n, m) = I_h(x, y) \text{rect}\left[\frac{x}{L_x}, \frac{y}{L_y}\right] \times \sum_{n=-\frac{N}{2}}^{\frac{N}{2}} \sum_{m=-\frac{M}{2}}^{\frac{M}{2}} \delta(x - n\Delta x, y - m\Delta y), \quad (3)$$

where n, m are integer numbers that define the pixel position of the hologram, $\Delta x, \Delta y$ are the

pixel size in the x and y directions (sampling increments). N, M are the number of pixels in the x and y directions and L_x, L_y are the dimensions of the CCD sensor. Numerical reconstruction is done by multiplying the digital hologram by a numerical model of the reference wave, typically a plane wave with an unitary amplitude is used (phase is constant all along the wave front) [11], then the numerical reconstructed hologram is the same as the numerical recorded hologram $h_h(n, m) = I_h(n, m)$.

For off-axis holography the virtual image, the real image and the non-diffracted wave are spatially separated [12]. Figure 2 shows the spatial frequencies space of $h_h(n, m)$ (Fourier space).

Fig. 2: Spatial separation of the diffraction orders.

We can easily filter the object information by applying a mask on the Fourier space:

$$h'_h(n, m) = \mathfrak{F}^{-1}\{\{\mathfrak{F}\{h_h(n, m)\}\}\text{mask}(k_n, k_m)\}, \quad (4)$$

where $h'_h(n, m)$ is the complex wave front of the object in the hologram plane, $\mathfrak{F}^{-1}$ and $\mathfrak{F}$ are the inverse Fourier transform and the Fourier transform, respectively. The filter is represented by $\text{mask}(k_n, k_m)$, with spatial frequencies k_n, k_m . The distribution of the object wave front in the object plane $h'_o(n, m)$ is obtained by the angular spectrum theory [13]:

$$h_o(\xi, \eta) = \mathfrak{F}^{-1}\left\{\left[\mathfrak{F}\{h(n, m)\} \times -\right. \right. \\ \left. \left. \times \text{mask}(k_n, k_m) e^{id\left(\sqrt{k^2 - k_n^2 + k_m^2}\right)}\right]\right\}, \quad (5)$$

where $k = 2\pi/\lambda$ is the wave number, λ is the optical source wavelength, and d is the distance between the object plane and the CCD plane.

When the image is focused onto the CCD camera, propagation is not needed; then distribution of the object wave can be obtained directly from numerical reconstruction on the CCD plane:

$$h_o(\xi, \eta) = h'_h(x, y) = \mathfrak{F}^{-1}\{\{\mathfrak{F}\{h_h(x, y)\}\}\text{mask}(k_n, k_m)\}. \quad (6)$$

Then the amplitude and phase are determined by:

$$A(\xi, \eta) = |h_o(\xi, \eta)|, \quad (7)$$

$$\phi(\xi, \eta) = \arctan\left(\frac{\text{Re}(h_o(\xi, \eta))}{\text{Im}(h_o(\xi, \eta))}\right). \quad (8)$$

Now, the thickness or height of the sample depends on the experimental setup (in this particular case optical reflection is considered as the investigated sample is a diffused object); it is calculated by:

$$\text{Thickness}_n(\xi, \eta) = \frac{\phi_n(\xi, \eta)\lambda}{4\pi}. \quad (9)$$

Dynamical process can be monitored by applying holographic interferometry concepts [14]. The first step consists in taking the initial state (base hologram); next holograms are taken at different times and each one represents the state of the sample at that specific time. For

quantifying partial variations as related to the original state, it is possible to calculate the phase difference between the base hologram and sequential holograms by the following equation:

$$\Delta\phi_n(\xi, \eta) = \arctan\left(\frac{\text{Im}\{h_i(\xi, \eta)h_n(\xi, \eta)\}}{\text{Re}\{h_i(\xi, \eta)h_n(\xi, \eta)\}}\right), \quad (10)$$

where $\Delta\phi_n(\xi, \eta)$ represent the partial phase variation concerned to the original state, $h_i(\xi, \eta)$ and $h_n(\xi, \eta)$ are the complex field distributions of the object at its initial state and its sequential states, respectively.

Now, partial thickness variations are obtained by the following Eq. (11):

$$\Delta\text{Thickness}_n(\xi, \eta) = \frac{\Delta\phi_n(\xi, \eta)\lambda}{4\pi}. \quad (11)$$

2. Experimental set-up

A piece of copper was polished to obtain a smooth surface (Fig. 3), and then the sample was wetted with a saline chloride solution and mounted on the experimental setup, at room conditions.

The experimental setup shown at Figure 4 is based on a modified Mach-Zehnder interferometer; an amplified, collimated optical beam emitted from a low power He-Ne laser is divided in two equal intensity beams (i.e. reference and object signals). The object signal is focused with a lens and a 4X microscopic objective onto the metallic sample, which reflected surface image is recaptured by the objective and focused in the CCD sensor. On the other hand the reference signal is directed by some mirrors and focused also to the camera; a digital hologram obtained by the interference between the two beams is stored in a PC. As in

Fig. 3: Copper sample.

Fig. 4: Experimental setup for digital holography.

Fig. 5: Quantification of corrosion products growth by means of DHM: a) beginning of test, b) 10 min, c) 20 min, d) 60 min, e) 10 hours and f) 18 hours.

this particular case the image is focused in the camera sensor plane there is no need to perform numerical propagation at different planes, and only numerical reconstruction is required to obtain a phase map in order to get 3D reconstruction at different moments; then partial variations of oxide layer growth formed on the copper sample due to corrosion process as a function of time are obtained.

Immediately after mounting the sample, first hologram was captured and consecutive holograms were captured every 30 seconds during the first 20 min, and after this every 5 min during 18 hrs.

3. Results

Once holograms were obtained at different times, the total oxide layer growth is obtained. Figure 5 shows a sequence of the 3D reconstruction obtained by means of digital holographic microscopy (DHM) at different times (phase unwrapping was made using the algorithm proposed by Richard M. Goldstein [15,16]). The presented sequence illustrates the oxide growth as a function of time, where red section represents the maximum thickness which is extending across metal surface as a function of wetness time, as expected. The lower section presents a notch acting as a visual reference mark to check optical focusing.

The monitoring of oxide layer growth taken at the surface sample central section, depending on the "x"-direction, and the same growth as a function of time obtained at a sole point centered at the sample, and shown at Fig. 6(a) and (b), respectively. It can be seen that oxide layer increases as a function of wetness time, but such oxide thickness growth rate tends to get lower until it reaches a steady state (Fig. 6(a)).

Figure 6(b) presents the dynamic oxide growth behavior, in which instabilities and variations in the oxide thickness were registered, probably associated to oxide removal or dissolution at the focal point. After six hours of wetness, the oxide thickness reached a steady

state and to an almost constant value, with only a few transients observed. This indicates that oxide growth is almost finished after six hours, and a film rupture/repassivation events process and film reformation takes place over local sites. The oxide layer reached a final 600 nm thickness.

Fig. 6: a) Lateral profiles obtained from the digital topographic reconstruction at different moments, b) oxide layer growth as a function of time..

4. Conclusions

A novel application of digital holographic microscopy as a non-destructive, non-contactive tool for optical monitoring of the oxide layer growth on a copper sample, during an electrochemical corrosion process, has been presented; it also shows the potentiality of these optical methods when they are used as alternative methods for the investigation of dynamic physical-chemical processes as metallic corrosion.

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