Interferometric Sensor for Electrochemical Studies of Metallic Alloys in Aqueous Solution

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In a previous study a mathematical model relating surface and bulk behaviors of metals in aqueous solution was developed. The model was established based on principles of holographic interferometry for measuring microsurface dissolution, i.e., mass loss, and on those of electrochemistry for measuring the bulk electronic current, i.e., corrosion current. In the present work, an interferometric sensor was built based on the above model, and the corrosion current density of coated copper and brass in seawater were obtained using this sensor. The interferometric sensor was also utilized for the first time to measure the initial stage of the anodization process (oxidation) of aluminium samples in aqueous solution. This was carried out chemically in different acid concentrations (3.125-25% H₂SO₄) at room temperature. The sensor was further used for observation of catalytic activities, i.e., pitting corrosion, which occurred subsequent to the anodization of the aluminium samples in aqueous solutions, after an oxide film had been formed.

Key words: holographic interferometry, corrosion, pitting corrosion, brass, copper, aluminium, seawater, sulphuric acid, organic coating, chemical anodization, Al₂O₃ oxide film

1. Introduction

In recent works published elsewhere,¹⁻⁵ different techniques of optical interferometry have been found very useful in many applications in the field of electrochemistry. For example, the technique of holographic interferometry was used to monitor the mechnanochemical behavior, i.e., stress corrosion cracking, corrosion fatigue, and hydrogen embrittlement of metallic electrodes in aqueous solutions.¹⁻⁵ The interferometry is used to measure microscopic deformation and electrochemical techniques to determine the corrosion current of metallic samples in aqueous solutions.

The objective of the present work was to monitor and measure corrosion of different metallic samples which have been coated in typical corrosive solutions using the technique of holographic interferometry. Furthermore, the work aimed to develop an interferometric sensor to measure specifically the corrosion current density of copper and brass samples coated with epoxy-based coating in seawater. Comparison between the corrosion data of the coated and uncoated samples was also made.

Recently the authors derived a mathematical model⁶⁻⁷ relating the thickness of cathodic deposition, i.e., mass gain or anodic dissolution, (that is mass loss), to the current density of a metal electrode. The model was established based on principles of holographic interferometry for measuring microsurface alterations and on those of electrochemistry for measuring the current density. The model can be utilized in this investigation to relate the orthogonal displacement of a coating film, due to the corrosion of the metal under the film, and to the corrosion current density of the based metal. It is described as follows:

\[ J = \frac{F|Z|du}{MT} \]  

where \( J \) is the corrosion current density of the based metal, \( F \) is Faraday’s constant, \( |Z| \) is the absolute number of electron charges, \( M \) is the atomic weight of the based metal, \( T \) is the time of the anodic current, \( u \) is the orthogonal displacement of the coating film, \( d \) is the density of the based metal.

Also, in the present work the thickness of anodized films of aluminium samples in sulphuric acid solutions was measured by the interferometric sensor. The initiation stage of the anodization phenomenon of the aluminium was monitored in a range of concentration of sulphuric acid solutions. The reason for the selection of aluminium samples for this investigation was because aluminium is known to be readily anodized not only by electrochemical methods but by chemical oxidation alone.⁸ In other words, a thicker oxide layer than the layer which the aluminium normally has in air can form by either an electrochemical or a chemical method.

2. Experimental

2.1 Measurement of Corrosion Underneath Coatings

Epoxy, a commercial organic coating was applied on one side of metallic samples of copper (99.7%) and brass (76% Cu & 24% Zn). The epoxy is polyamide cured (white) paint. A coal tar (black) epoxy (polyamide cured) was used on the other side of the samples. The reason behind covering these other sides with the coal tar epoxy was to protect them from the solutions while testing sample susceptibility to corrosion under the the polyamide cured (white) paint. The samples were fabricated in a plate form with dimensions of 10.0 cm x 10.0 cm x 0.15 cm. At the beginning of each test, a sample of the coated copper and
brass was immersed in the local seawater of Kuwait for 1 h. While the sample was in the solution, the corrosion potential was measured by a potentiometer with respect to the saturated calomel electrode (SCE), a reference electrode. After the first hour of immersion, a hologram of the sample was recorded using an off-axis holography (see Fig. 1 for the optical setup). A camera with a thermoplastic film (HC-300 Thermoplastic Recorder made by Newport Corporation) was used to facilitate recordings of the holographic interferometry of the samples. For more details on the optical setup of the experiment, the reader is encouraged to refer to literature elsewhere. During each experiment, the holographic interferograms were recorded as a function of time; each test lasted for 60 min. Then, the interferograms were used to calculate an orthogonal displacement, i.e., anodic dissolution or deposition, of the surface of the metal, and the displacement measurements were used to determine the thickness of the anodized films of the samples in 3.125-25% H₂SO₄ solution.

3. Results and Discussion

3.1 Measurement of Corrosion Underneath Coatings

In this investigation, interferograms were observed on the coated samples of both metals. The interferograms were similar to the one observed on a coated carbon steel tested in tap water. Using the data from the obtained interferograms, one can develop the relationship between the corrosion of samples under the coating and the elapsed time of the experiment. Figure 2 shows a plot of the corrosion current density \( J \) versus the elapsed time of the experiment for the coated and uncoated copper in seawater. The corrosion current density \( J \) of the copper