

Optical Interferometry as Electrochemical Emission Spectroscopy of Metallic alloys in Aqueous Solutions

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Holographic interferometry, an electromagnetic method, was used to study corrosion of carbon steel, aluminum and copper nickel alloys in NaOH, KCl and H₂SO₄ solutions respectively. The technique, called electrochemical emission spectroscopy, consisted of in-situ monitoring of changes in the number of fringe evolutions during the corrosion process. It allowed a detailed picture of anodic dissolution rate changes of alloys. The results were compared to common corrosion measurement methods such as linear polarization resistance measurements and electrochemical impedance spectroscopy. A good agreement between both data was found, thus indicating that holographic interferometry can be a very powerful technique for in-situ corrosion monitoring.

Keywords : *holographic interferometry, electrochemical impedance spectroscopy (E.I.S), electrochemical-emission spectroscopy, linear polarization, corrosion, He-Ne laser light.*

1. Introduction

In recent works conducted by the author,¹⁾⁻¹⁶⁾ an optical transducer was developed for materials testing and evaluation of different electrochemical phenomena. The optical transducer was developed based on incorporating methods of holographic interferometry for measuring microscopic deformations and electrochemical techniques for determining electrochemical parameters of samples in aqueous solutions. In addition to the optical transducer being as an electrometer for measuring different electrochemical parameters but also, it was used as a 3D-interferometric microscope for detecting different microalterations at a metal surface in aqueous solution, at a microscopic scale. In previous studies, the optical transducer was applied successfully in determining the mechano-chemical properties in aqueous solutions by detecting micro-deformations and measuring the corresponding current density by the optical transducer.¹⁾⁻⁵⁾ It was also used as an optical corrosion-meter⁶⁾⁻⁸⁾ by measuring:

- cathodic deposition and anodic dissolution layers of metals in aqueous solutions.
- cathodic and anodic current densities which correspond to the cathodic deposition and anodic dissolution layers, respectively.
- uniform corrosion and localized corrosion on metal

surfaces and on substrates covered by organic coatings or under crevice assemblies.⁸⁾⁻¹⁴⁾

It was also used to document adsorption and desorption phenomena of chemical species on metal surfaces in aqueous solutions.¹²⁾ Finally, the optical transducer was applied as an electrometer for measuring the double layer capacitance, the alternating current impedance and the corresponding oxide layer thickness of metals in aqueous solution.¹⁵⁾⁻¹⁶⁾

The objective of the present work was to determine the rate change of the number of the fringe evolutions during the corrosion test of carbon steel, aluminum and copper nickel alloys in NaOH, KCl and H₂SO₄ solutions, respectively. The technique, called electrochemical emission spectroscopy, consisted of in-situ monitoring of changes in the number of fringe evolutions during the corrosion process. It allowed a detailed picture of anodic dissolution rate changes of alloys. The results were compared to common corrosion measurement methods such as linear polarization resistance and electrochemical impedance spectroscopy.¹⁷⁾ A good agreement between both data was found thus indicating that holographic interferometry can be a very powerful technique for in-situ corrosion .

2. Theoretical analysis

In a mathematical relationship derived by the author

elsewhere,^{7,8)} one can measure the corrosion current density (J) of metallic samples in aqueous solutions according to the following mathematical model:^{7)&8)}

$$J = \frac{F |Z| DU}{MT} \quad (1)$$

Where J is the corrosion current density of the based metal.

F is Faraday's constant.

$|Z|$ is the absolute number of electron charge.

M is the atomic weight of the sample material.

T is the time of the anodic current.

D is the density of the based metal.

U is the orthogonal displacement of metal surface due to corrosion, where

$$U = N \lambda / (\sin \alpha + \sin \beta) \quad (2)$$

Where N is the number of fringes.

λ is the wavelength of the laser light used in the experiment

α is the illumination angle

β is the viewing angle, both α and β can be obtained from the set up of the experiment.

A detail derivation of equation 1 and 2 is given elsewhere in literature.^{7)&8)}

Equation No.1 describes the relationship between the corrosion current density, J , and the orthogonal displacement of metal surface due to corrosion, U . In other words, one can measure the corrosion current density of the base metal by knowing the thickness of the orthogonal displacement of metal surface due to corrosion. The thickness of the orthogonal displacement, U , can be measured by holographic interferometry from equation No. 2. Therefore, one can correlate the number of the fringe evolutions, N , to the corrosion current density, J . By applying equation No. 1, one can detect the electrochemical-emission spectroscopy of all metallic samples in solutions by holographic interferometry. This can be achieved by plotting dN versus the elapsed time of the experiment, where dN is the difference between the number of the fringe evolutions of two subsequent readings of the number of fringe evolutions. By plotting dN versus time, this will definitely reflect the abrupt rate change, electrochemical-emission spectroscopy, of the anodic dissolution behaviors of the metallic samples as a function time of the corrosion test.

3. Experimental details

Metallic samples of a carbon steel (0.45% Mn, 0.25% Si, 0.2C%, and 99.1% Fe), pure aluminium (99% Al), and copper-nickel based alloy (70% Cu and 30% Ni) were used in this investigation. Samples of all metallic alloys were fabricated in two different sizes of a circular shape. The large size has a dimension of 9 cm in a diameter and a total surface area of 63.617 cm², which were used for the holographic interferometry test. The small size samples have a dimension of 1.4 cm in diameter and surface area of 1.54 cm², which were used in the other electrochemical tests. Then, all large samples (9 cm in diameter) were covered by a black epoxy (polyamide tar) except one side of the samples. The reason behind covering the samples by the black epoxy is to isolate the surface area of the samples from contacting the seawater, while testing the bare side of the samples to corrosion in aqueous solutions. At the beginning of each test, the sample was immersed in an aqueous solution for nearly 45 minutes. While the sample was in the solution the corrosion potential was monitored by a potentiometer with respect to the Saturated Calomel Electrode (SCE), a reference electrode, until the steady state potential reached. The carbon steel, pure aluminium, and copper-nickel based alloy samples were tested in the 1M NaOH (pH = 13.2), 1M KCl (pH = 4.8), and 1M H₂SO₄ (pH = 1.27), respectively, at the open circuit potentials of the samples in solutions. Then a hologram of the sample was recorded using an off axis holography, see Fig. 1 for the optical set up. In this study, a camera with a thermoplastic film was used to facilitate recordings of the real time-holographic interferometry of the samples during the corrosion test. The camera is HC-300 Thermoplastic Recorder made by Newport Cor

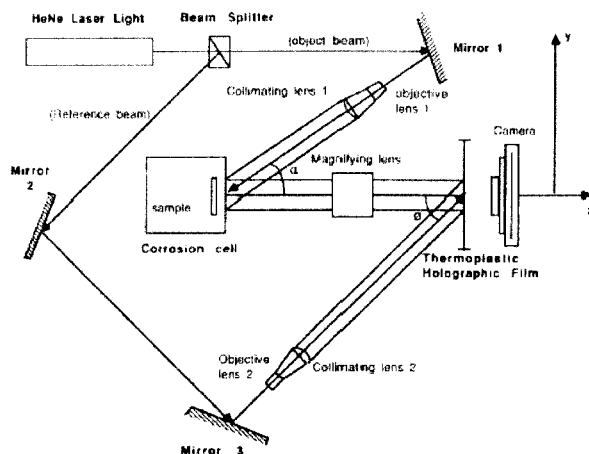


Fig. 1. Optical setup of an off axis holographic interferometry.

poration. For more details on the procedures of the experiment, the reader is encouraged to refer to literature elsewhere.^{7)&8)} Furthermore, the linear polarization and the electrochemical impedance measurements were recorded for all metallic alloys in various solutions, by using the small size samples. The linear polarization and the A.C-impedance measurements were conducted by using the ACM Gill 8AC impedance system. The obtained data of the electrochemical impedance measurements were basically Nyquist plots,¹⁷⁾ plot of the real alternating current impedance (z') versus the imaginary alternating current impedance (z''). Fig. 2 shows an example of Nyquist plot of copper-nickel based alloy sample in 1M H_2SO_4 . By using Nyquist plots, such as the one in Fig. 2, a number of electrochemical parameters of samples of the carbon steel, pure aluminium, and copper-nickel based alloy in the 1M NaOH, 1M KCl, and 1M H_2SO_4 solutions, respectively, can be determined. But the most significant parameter for this investigation is the polarization resistance of the metallic samples in solutions. This is because from the polarization resistance values from linear polarization or electrochemical impedance measurements, the corrosion current density can be determined.¹⁸⁾ Fig. 3 shows an example of the linear polarization plot of the copper-nickel based alloy sample in 1M H_2SO_4 . It is worth mentioning that in each experiment, the holographic interferograms were recorded as a function of time, in which each test lasted for 60 minutes, at room temperature. Then, the difference between the number of the fringe evolutions of two subsequent numbers of the fringe evolutions, dN , were plotted as a function time in order to show the abrupt rate change of electrochemical-emission spectroscopy of the metallic samples in solutions. The abrupt rate change of electrochemical-emission spectroscopy was recorded each consecutive 5 minutes of the elapsed time the experiment.

4. Results and discussion

Figs. 4a, b, c shows an example of progressive interferograms of a copper-nickel sample in 1M H_2SO_4 solutions as a function of time. Fig. 4a represents a real-time interferogram of the sample after 2 minutes of the elapsed time of the corrosion test, where 1 fringe appeared on the photograph. This indicates that the copper-nickel sample has oxidized in a microscopic scale after a couple minute of the sample immersion in 1M H_2SO_4 . Figs. 4b, c are the same interferogram after 3, and 35 minutes of elapsed time of the corrosion test, where 3 and 4 fringes detected on the photograph, respectively. It is obvious from these interferograms, photographs, that

there is a localized chemical oxidation, depicted by the interferometric patterns, in Figs. 4b, c in which a localized

interferometric perturbation appeared on the upper right corner of Figs. 2b, c. These observations of Figs. 4b, c are in agreement with interferograms documented for pitting corrosion of a pure copper sample tested during cyclic polarization in tap water.¹³⁾ It is worth mentioning that each fringe in Fig. 4 (dark line) accounts to an orthogonal displacement equivalent to $0.3 \mu\text{m}$ according to mathematical models reported elsewhere.⁷⁾⁻⁸⁾ In other words, holographic interferometry can be used as a powerful tool, interferometric microscope, in the field of electrochemistry.

By using data from interferograms such as those in Fig. 4, one can develop a relationship between the difference of the number of the fringe evolutions of two subsequent fringe numbers and the elapsed time of the experiment. Figs. 5, 6 & 7 show plots of the difference between the number of the fringe evolutions of two subsequent fringe numbers and the elapsed time of the experiment of the carbon steel, pure aluminium, and copper-nickel based

alloy in 1M NaOH, 1M KCl, and 1M H₂SO₄ solutions, respectively. From Figs. 5, 6 & 7, one can determine the abrupt rate change of electrochemical-emission spectroscopy of the carbon steel, pure aluminium, and copper-nickel based alloy in 1M NaOH, 1M KCl, and 1M H₂SO₄ solutions, respectively. For instance, Fig. 5 shows the rate change of the difference between the number of the fringe evolutions of the carbon steel in the 1M NaOH. It obvious from Fig. 5 that the rate change of electrochemical-emission spectroscopy of the carbon steel was observed to decrease initially in a gradual manner from $dN = 7$ fringes to $dN = 0$ fringe per minute, from the beginning of the test to the 10 minutes of the elapsed time of the experiment. This behavior of the electrochemical-emission spectroscopy of the carbon steel in the 1M NaOH indicates that the corrosion rate of the carbon steel samples was continuously decreasing as a function of time. In contrast, a number of abrupts of the fringe evolution (ranging from $dN = 1$ to $dN = 0$) was observed at 20, 30, 45, 55 minutes from 20 to 60 minutes of the elapsed time of the experiment, see Fig. 5. This behavior can be contributed to the unstable film formation at the carbon steel in the 1M NaOH. However, the range of the abrupts of the fringe evolution, from $dN = 1$ to $dN = 0$ during the last 40 minutes of the elapsed time of the experiment, can be considered that the carbon steel has attained a steady rate change of electrochemical-emission spectroscopy after the initial rate change decrease. On the other hand, the rate change of electrochemical-emission spectroscopy of the pure aluminium in 1M KCl was observed to decrease drastically from $dN = 5$ fringes to a steady state value of $dN = 0$ fringe per minute till the end of the test, see Fig. 6. It is obvious from Fig. 6 that the pure aluminium is more stable in 1M KCl, less chemically active, than the carbon steel in 1M NaOH. This is due to the fact that there is no abrupt rate

change in the fringe evolution observed in the electrochemical emission spectroscopy, Fig. 6, of the pure aluminium in 1M KCl. In addition, Fig. 7 shows the rate change of the difference between the number of the fringe evolutions of the copper-nickel in the 1M H₂SO₄. It obvious from Fig. 7 that the rate change of electrochemical-emission spectroscopy of the copper-nickel was observed to decrease initially in a gradual manner from $dN = 4$ fringes to $dN = 0$ fringe per minute, from the beginning of the test to the 10 minutes of the elapsed time of the experiment. Then the copper-nickel sample was observed to attain a steady rate change of the difference between the number of the fringe evolution from 10 to the end of the elapsed time of the experiment, $dN = 0$, except a sudden abrupt rate change of fringe evolution ($dN = 1$) was observed at 45 minutes from the elapsed time of the experiment. This electrochemical behavior of the copper-nickel in 1M H₂SO₄ can be explained due to a localized chemical attack. Also, the electrochemical behavior of the copper-nickel in 1M H₂SO₄ is in agreement with interferograms in Figs. 4b, c in which a localized interferometric perturbation was observed on the upper right corner of Figs. 4b, c, indicating the presence of a localized chemical attack.

In general, from Figs. 5, 6 & 7 one can predict that the pure aluminium (in 1M KCl) is less active chemically than the carbon steel (in 1M NaOH) and copper-nickel (in 1M H₂SO₄). Furthermore, measurements of the corrosion current density of all metallic alloys by the linear polarization method and electrochemical impedance spectroscopy confirmed that the pure aluminium is less active chemically (in 1M KCl) than the carbon steel (in 1M NaOH) and copper-nickel (in 1M H₂SO₄). The corrosion current density of the pure aluminium was found $3.18 \mu\text{A}/\text{cm}^2$ and $2.82 \text{mA}/\text{cm}^2$ by the linear polarization and the electrochemical impedance spectroscopy, respectively. In contrast, the corrosion current density of the carbon steel was found $6.19 \mu\text{A}/\text{cm}^2$ and $4.48 \text{mA}/\text{cm}^2$ by the linear polarization and the electrochemical impedance spectroscopy, respectively. On the other hand, the corrosion current density of the copper-nickel was found $9.25 \mu\text{A}/\text{cm}^2$ and $20.52 \text{mA}/\text{cm}^2$ by the linear polarization and the electrochemical impedance spectroscopy, respectively.

5. Conclusions

The following conclusions are drawn from the above investigation:

1. Electrochemical Emission Spectroscopy based on holographic interferometry was found a very powerful technique for in-situ corrosion monitoring.

2. comparison between data obtained from the common corrosion measurement methods such as linear polarization resistance and electrochemical impedance spectroscopy was found in a good agreement electrochemical emission spectroscopy.

3. In general, from electrochemical emission spectroscopy, Figs. 5, 6 & 7 one can predict that the pure aluminium (in 1M KCl) is less active chemically than the carbon steel (in 1M NaOH) and copper-nickel (in 1M H₂SO₄).

4. Measurements of the corrosion current density of all metallic alloys by the linear polarization method and Electrochemical Impedance Spectroscopy ((E.I.S) confirmed that the pure aluminium is less active chemically (in 1M KCl) than the carbon steel (in 1M NaOH) and copper-nickel (in 1M H₂SO₄).

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