King Saud University

Journal of Saudi Chemical Society

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ORIGINAL ARTICLE

Surface resistivity/conductivity of oxide–hydroxide compounds in inhibited seawater by optical interferometry

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Abstract Optical interferometry techniques were used to measure the surface resistivity/conductivity of carbon steel samples in blank seawater and in seawater with different concentrations of a corrosion inhibitor, without any physical contact. The measurement of the surface resistivity/conductivity of carbon steel samples was carried out in blank seawater and in seawater with a concentration range of 5–20 ppm of RA-41 corrosion inhibitor, at room temperature. In this investigation, the real-time holographic interferometry was carried out to measure the thickness of anodic dissolved layer or the total thickness, Utotal, of the formed oxide layer of carbon steel samples during the alternating current (AC) impedance of the samples in blank seawater and in 5–20 ppm RA-41 inhibited seawater, respectively. In other words, the surface resistivity/conductivity of carbon steel samples was determined simultaneously by holographic interferometry, an electromagnetic method, and by the Electrochemical Impedance (E.I) spectroscopy, an electronic method. In addition, a mathematical model was derived in order to correlate between the AC impedance (resistance) and to the surface (orthogonal) displacement of the surface of the samples in solutions.

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1. Introduction

It is well known that conventional methods of measuring the surface resistivity/conductivity of carbon steel samples were based on direct current (DC) electrochemical methods, for samples of known oxide film thickness (Uhlig, 1971). There are dis-

advantages of using the DC electrochemical methods for measuring the surface resistivity/conductivity of carbon steel samples as compared to electromagnetic methods, i.e., holographic interferometry, with applications of the EIS technique (AC method) for the anodic dissolution process. The DC electrochemical methods are known to produce heat that might affect the measurements of the surface resistivity/conductivity of samples of high resistive oxide films such as anodized aluminum samples, metallic samples in high resistive environments, and metallic samples in inhibited solutions (Uhlig, 1971), like the present case. Therefore, a better approach of avoiding erroneous measurements of the surface resistivity/conductivity of samples is proposed in the present work. Electromagnetic methods,

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i.e., holographic interferometry, with applications of the EIS technique (AC method) was proposed for avoiding the erroneous measurements of the surface resistivity/conductivity of samples of high resistive oxide films such as anodized aluminum samples, metallic samples in high resistive environments, and metallic samples in inhibited solutions (Uhlig, 1971), like the present case. The DC electrochemical methods can measure the surface resistivity/conductivity of carbon steel samples only after the completion of the anodic dissolution processes of the carbon steel in solutions. In contrast, the holographic interferometry, with applications of the EIS technique (AC method), can measure the surface resistivity/conductivity of carbon steel samples in situ during the anodic dissolution processes. Also, holographic interferometry, with applications of the EIS technique (AC method), is a powerful 3D-microscope for monitoring the surface of carbon steel samples during the anodic dissolution processes, in a microscopic scale.

In a previous work conducted by the author (Habib, 2004), a mathematical model was derived in order to relate the electrical resistance of the oxide film on a solid metal sample to the thickness of the oxide film on the metal sample. The mathematical model can be described as the following:

$$R = \rho U_{total}/A \tag{1}$$

where, R is the direct current (DC) resistance of the oxide film, Ohm. ρ is the electrical resistivity of the oxide film, Ohm-cm. A is the exposed surface area of the sample to solution, $37.5 \, cm^2$. U_{total} is the total thickness of the oxide film which can be obtained by holographic interferometry, a non-contact technique, μm. U_{total} can be determined as the following:

$$U_{total} = N\lambda/(\sin\alpha + \sin\beta) \tag{2}$$

where, N is the number of fringes. λ is the wavelength of the laser light used in the experiment, for He–Ne laser light, $\lambda = 0.6234 \, \mu m$. α is the illumination angle, $\alpha = 51.2°$. β is the viewing angle, $\beta = 90°$, both α and β can be obtained from the set up of the experiment. A detailed derivation of Eqs. (1) and (2) is given elsewhere in the literature (Habib, 1993; Habib et al., 1997). Eq. (1), can be used to determine the surface resistivity/conductivity of carbon steel samples in aqueous solution without any physical contact. This can be achieved by substituting the alternating current (AC) impedance (Z) in the place of the direct current (DC) resistance (R) in Eq. (1). The substitution of the value of Z in the place of the value of R is valid when the Z value was measured by the technique of electrochemical impedance spectroscopy (EIS), at very low frequency, at room temperature (EG&G, 1982). In other words, Eq. (1) can be rewritten in a modified version of the following form;

$$|Z| = \rho U_{total}/A \tag{3}$$

where; ρ is the electrical resistivity of the formed oxide layer of carbon steel samples in inhibited seawater, Ohm-cm. U_{total} is the total thickness of the formed oxide layer of carbon steel samples in inhibited seawater. Or, U_{total} is the total thickness of the anodic dissolved layer of carbon steel samples in blank seawater, which can be obtained by holographic interferometry, μm.

In this investigation, Eq. (3) was used for the first time to determine the surface resistivity/conductivity of the carbon steel samples, along with the applications of the EIS technique for the anodic dissolution processes, in blank seawater and in seawater with a concentration range of 5–20 ppm of RA-41 corrosion inhibitor, at room temperature. In addition, Eq.

(3) was used with the assumption that U_{total} is the total thickness of the formed oxide layer of carbon steel samples in inhibited seawater or, U_{total} is the total thickness of the anodic dissolved layer of carbon steel samples in blank seawater. So, one can measure the total thickness of the formed oxide layer, U_{total}, of carbon steel samples in 5–20 ppm RA-41 inhibited seawater solutions or the thickness of the anodic dissolved layer of carbon steel samples in blank seawater, from Eq. (2). In the mean time, the alternating current (AC) impedance (Z) of the carbon steel samples can be determined by the technique of electrochemical impedance spectroscopy (EIS) during the anodic dissolution processes in solutions. Eventually, a correlation can be developed between the determined (AC) impedance (Z) (from EIS) and the total thickness of the formed oxide layer, (U_{total}), of samples (by holographic interferometry), from Eq. (3). So, a proportionality constant (surface resistivity = ρ or surface conductivity = $1/\rho = \sigma$) between the determined (AC) impedance (Z) and the total surface displacement (by holographic interferometry) can be obtained, without any physical contact with least erroneous measurements.

2. Experimental works

Metallic samples of carbon steel, UNS No. 1020, were used in this investigation. The chemical composition of the carbon steel is 0.18–0.23% C, 0.3–0.6% Mn, and balanced Fe. The carbon steel samples were fabricated in a rectangular form with dimensions of $5 \, cm \times 10 \, cm \times 0.15 \, cm$. Then, all samples 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 seawater. At the beginning of each test, the carbon steel sample was immersed in an aqueous solution for nearly 45 min. While the sample was in the solution the corrosion potential was monitored by a potentiometer with respect to the Saturated Colomel Electrode (SCE), a reference electrode, until the steady state

Table 1 Chemical composition of blank seawater.

Parameter	Maximum (ppm)	Minimum (ppm)	Normal seawater (ppm)
Sodium	12433	11536	11860
Magnesium	1543	1490	1340
Potassium	459	469	410
Calcium	404	378	515
Copper	0.05	<0.05	–
Zinc	0.05	<0.05	–
Iron	0.5	<0.05	–
Manganese	0.1	<0.05	–
Chloride	22014	21933	20959
Sulfate	3272	3200	2650
Bicarbonate	161	156	130
Ammonia	1.13	0.02	–
Nitrate	0.025	0.002	–
Sulfide	0.2	0.005	–
Total Organic Carbon	8	8	–
	–	–	–
Total HC	0.327	0.204	–
Silica	0.09	0.05	–
TDS	46300	44100	35840
Bromide	80	–	66
Floride	1.25	–	1.3