

Measurement of Surface Resistivity and Surface Conductivity of Anodized Aluminium by Optical Interferometry Techniques

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Abstract

Optical interferometry techniques were used for the first time to measure the surface resistivity and surface conductivity of anodized aluminium samples in aqueous solution, without any physical contact. The anodization process (oxidation) of the aluminium samples was carried out in different sulphuric acid solutions (1.0-2.5 % H₂SO₄), by the technique of electrochemical impedance spectroscopy (EIS), at room temperature. In the mean time, the real-time holographic interferometric was carried out to measure the thickness of anodized (oxide) film of the aluminium samples during the anodization process. Then, the alternating current (AC) impedance (resistance) of the anodized aluminium samples was determined by the technique of electrochemical impedance spectroscopy (EIS) in different sulphuric acid solutions (1.0-2.5 % H₂SO₄) at room temperature. In addition, a mathematical model was derived in order to correlate between the AC impedance (resistance) and to the surface (orthogonal) displacement of the samples in solutions. In other words, a proportionality constant (surface resistivity or surface conductivity=1/ surface resistivity) between the determined AC impedance (by EIS technique) and the orthogonal displacement (by the optical interferometry techniques) was obtained. Consequently the surface resistivity (ρ) and surface conductivity (σ) of the aluminium samples in solutions were obtained. Also, electrical resistivity values (ρ) from other source were used for comparison sake with the calculated values of this investigation. This study revealed that the measured values of the resistivity for the anodized aluminium samples were 2.8×10^9 , 7×10^{12} , 2.5×10^{13} , and 1.4×10^{12} Ohms-cm in 1.0%, 1.5%, 2.0%, and 2.5 % H₂SO₄ solutions, respectively. In fact, the determined value range of the resistivity is in a good agreement with the one found in literature for the aluminium oxide, 85% Al₂O₃ (5×10^{10} Ohms-cm in air at temperature 30C⁰), 96% Al₂O₃ (1×10^{14} Ohms-cm in air at temperature 30C⁰), and 99.7% Al₂O₃ ($> 1 \times 10^{14}$ Ohms-cm in air at temperature 30C⁰).

Keywords: Electrical Resistivity, Electrical Conductivity, Alternating Current (AC) Impedance (Resistance), Holographic Interferometry, Aluminium, Oxide Aluminium (Al₂O₃), Room Temperature, and Sulphuric Acid Solution.

1.Introduction

It is well known that conventional methods of measuring the surface resistivity and surface conductivity of anodized aluminium samples were based on direct current (DC) electrochemical methods, for samples of known oxide film thickness [1]. There are disadvantages of using the DC electrochemical methods for measuring the surface resistivity and surface conductivity of anodized aluminium samples as compared to electromagnetic methods ,i.e., holographic interferometry, with the applications of the EIS technique (AC method) for the anodization process. The DC electrochemical methods are known to produce heat that might affect the measurements of the surface resistivity and surface conductivity of samples of high resistive oxide films such as anodized aluminium samples, metallic samples in high resistive environments, and metallic samples in inhibited solutions[1]. Therefore, a better approach of avoiding erroneous measurements of the surface resistivity and surface conductivity of samples is proposed in the present work. Electromagnetic methods ,i.e., holographic interferometry, with the applications of the EIS technique (AC method) was proposed for avoiding the erroneous measurements of the surface resistivity and surface conductivity of samples of high resistive oxide films such as anodized aluminium samples, metallic samples in high resistive environments, and metallic samples in inhibited solutions[1]. The DC electrochemical methods can measure the surface resistivity and surface conductivity anodized aluminium samples only after the completion of the anodization process of the aluminium. In contrast, the holographic interferometry, with the applications of the EIS technique (AC method), can measure the surface resistivity and surface conductivity of anodized aluminium samples in situ during the anodization process, during the growth of the oxide films in acid solutions. Also, holographic interferometry, with the applications of the EIS technique (AC method), is a powerful 3D-microscope for monitoring the surface of aluminium samples during the anodization process, in a microscopic scale.

In a previous work conducted by the author [2], 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 surface area of the sample, 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:

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

Where,

N is the number of fringes.

λ is the wavelength of the laser light used in the experiment, for He-Ne laser light, $\lambda = 0.6234 \mu\text{m}$.

α is the illumination angle, $\alpha = 47.23^\circ$.

β is the viewing angle, $\beta = 90^\circ$, 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 literature [3,4].

Equation No.1, can be used to determine the surface resistivity and surface conductivity of anodized aluminium (oxidized) 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 Equation No.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 [5].

In other words, Equation No.1 is rewritten to a modified version of the following form;

$$|Z| = \rho U_{\text{total}} / A \quad (3)$$

In this investigation, Equation No.3 was used for the first time to determine the resistivity of the anodized aluminium samples, along with the applications of the EIS technique for the anodization process. This due to the fact that the aluminium oxide is well known to have high resistivity values [1]. So, one can measure the total surface orthogonal displacement, U_{total} , of aluminium samples in solutions, from Equation No.2. Then, the alternating current (AC) impedance (Z) of the anodized aluminium samples can be determined by the technique of electrochemical impedance spectroscopy (EIS) during the anodization process in solutions. Eventually, a correlation can be developed between the determined (AC) impedance (Z)

(from EIS) and the total thickness of the oxide film (U_{total}) of samples (by holographic interferometry), from Equation No.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 the optical interferometry techniques) can be obtained, without any physical contact.

2.Experimental works

Metallic samples of a pure aluminium (99.7%) were used in this investigation. The aluminium samples were fabricated in a rectangular form with dimensions of 10.0 cm x 5.0 cm x 0.15 cm. Then, all samples were polished and ground by silicon carbide papers until the finest grade (1200 grade) reached. In order to be sure that the aluminium samples have attained scratches free surface, the samples were etched by a chemical solution for 2 minutes at a temperature ranged between 85-95C°. The etching solution made of 3 grams/liter of sodium hydroxide + 30 grams/liter of tri-sodium phosphate. Then a coal tar (black) Epoxy (polyamide cured) was used on one side and all edges of the samples. The reason behind covering one side and all the edges of the samples by the coal tar Epoxy is for protection from the solutions while anodizing the other side of the samples. At the beginning of each test, the aluminium sample first was immersed in the acid solution. 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 holographic interferometry of the samples. The camera is HC-300 Thermoplastic Recorder made by Newport Corporation. After the sample attained steady state corrosion potential, a hologram of the sample was recorded using an off axis holography, see Fig.1 for the optical set up. In the meantime, E.I. spectroscopy measurements were conducted using EG&G [5] Potentiostat/Galvanostat Mode 1273 with lock-in amplifier Model 5210 to obtain impedance spectra. All E.I. spectroscopy measurements were performed against a saturated calomel electrode (SCE) according to procedures described elsewhere [6]. During each experiment, the holographic interferograms were recorded as a function of time during the E.I.spectroscopy measurements, in which each test lasted for less than 60 minutes. Then, the interferograms were interpreted to an orthogonal displacement, i.e. anodization process, of the surface of the metal by using Equation No.2. Thereafter, the displacement measurements were

used to determine the thickness of the anodized films of the samples in 1.0-2.5 % H_2SO_4 solutions. Finally the A.C impedance (Z) values of the anodized films were determined by the E.I. spectroscopy technique in 1.0-2.5% H_2SO_4 , using Bode and Nyquist diagrams, respectively [5]. Eventually, a correlation was made between the determined (AC) impedance (Z) (from EIS) and the surface (orthogonal) displacement (U_{total}) of samples (by holographic interferometry), from Equation No.3. In other words, a proportionality constant (Surface Resistivity= ρ or surface conductivity= $1/\rho=\sigma$) between the determined (AC) impedance (Z) and the total surface displacement (by the optical interferometry techniques) was determined. Also, the obtained interferograms were used to show that a uniform anodization, i.e. oxidation, took place on the aluminium samples during the anodization process by E.I. spectroscopy measurements.

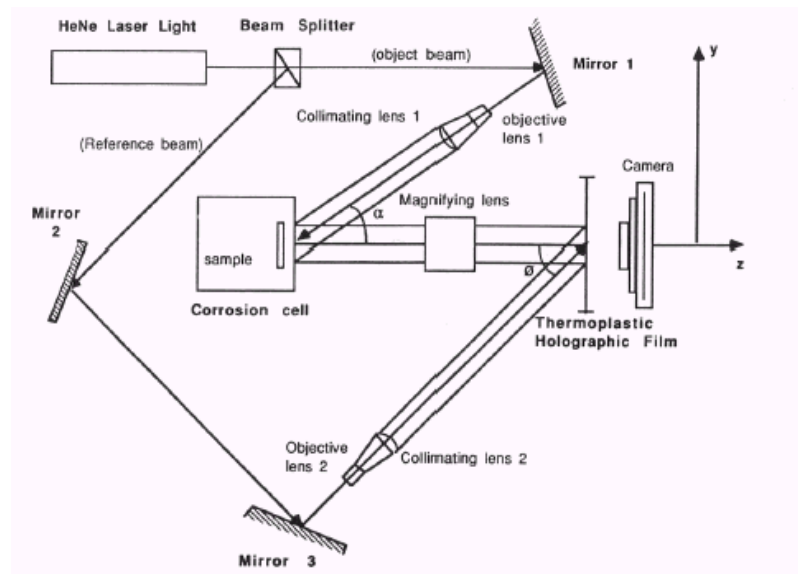


Fig.1. Optical setup of an off axis holographic interferometry.

3. Results and Discussion

Figure 2a-d show progressive interferograms of an aluminium sample anodized in 1.0 % H_2SO_4 solution as a function of time. Figure 2a represents a real-time interferogram of the sample at the beginning of the test (E.I. spectroscopy measurement), where 7 fringes appeared on the photograph. This indicates that the aluminium sample has rapidly anodized (oxidized) as soon as the sample immersed in the solution. Figure 2b is the same interferogram after 2 minutes of elapsed time, where 15 fringes detected on the photograph. It is obvious from this photograph

that there is a general chemical oxidation, depicted by the uniform interferometric pattern. Figure 2c is the same interferogram after 5 minutes, where 24 fringes recorded on the photograph. Figure 2d is the same interferogram after 8 minutes, where 33 fringes recorded on the photograph. It is worth mentioning that each fringe in Fig. 2 (dark line) accounts to an orthogonal displacement equivalent to $0.3\mu\text{m}$ according to mathematical models reported elsewhere [3-4]. In other words, holographic interferometry can be used as a 3D-interferometric microscope in the field of electrochemistry during different electrochemical measurements.

In the mean time, the A.C impedance (Z) values of the anodized aluminium were determined from Bode plots [5] at a frequency is equal to $f = 0.16$ Hz (at angular velocity $\omega = 1$ rad/sec.), where, $\omega = 2\pi f$. Bode plots are basically the logarithm of impedance (Z) and phase angle (θ) plotted versus the logarithm of frequency, Figure 3ab shows an example of Bode and Nuquist diagrams of the aluminium sample in 1.0 % H_2SO_4 , respectively.

Values of A.C. impedance obtained by electrochemical impedance spectroscopy (E.I.S) are given in Table 1 with respect to the final thickness of the oxide films, $19.91\mu\text{m}$, $21.72\mu\text{m}$, $42.72\mu\text{m}$, $43.1\mu\text{m}$ for anodized aluminium samples in 1.0%, 1.5%, 2.0%, and 2.5%, H_2SO_4 Solutions, respectively. Eventually, a correlation was made between the determined AC impedance (Z) (from EIS) and the surface (orthogonal) displacement (U_{total}) of samples (by holographic interferometry), from Equation No.3. Consequently, a proportionality constant (surface Resistivity= ρ or surface conductivity= $1/\rho = \sigma$) between the determined (AC) impedance (Z) and the total surface displacement (by the optical interferometry techniques) was determined. The determined values of the resistivity= ρ and conductivity= $1/\rho = \sigma$ of the anodized aluminium samples in different solutions are given in Table 1.

Table 1 shows that as the thickness of the oxide film increases, the A.C impedance increases first as well, then the A.C impedance attains a steady value as a function of the concentration of the H_2SO_4 solution. This observation is in agreement with the known electrochemical concept [1-2] of as the thickness of the oxide layer increases, the resistance (impedance) of the metal increases as well, because the oxide film protects (shields) the base metal from the surrounding environment. Likewise, this is a true for the values of the resistivity as a function of the concentration of the H_2SO_4 solution due to the direct proportionality of the resistivity with respect to the A.C impedance. In general, the determined values of the resistivity is ranged between 2.8×10^9 Ohms-cm for the anodized samples in 1% H_2SO_4 to 2.5×10^{13} Ohms-cm for the

anodized samples in 2% H₂SO₄. Also, electrical resistivity values (ρ) from other source [7] were used for comparison sake with the calculated values of this investigation. This study revealed that the measured value of the resistivity for the anodized aluminium samples were 2.8×10^9 , 7×10^{12} , 2.5×10^{13} , and 1.4×10^{12} Ohms-cm in 1.0%, 1.5%, 2.0%, and 2.5 % H₂SO₄ solutions, respectively. In fact, the determined value range of the resistivity is in a good agreement with the one found in literature [7] for the aluminium oxide, 85% Al₂O₃ (5×10^{10} Ohms-cm in air at temperature 30C⁰), 96% Al₂O₃ (1×10^{14} Ohms-cm in air at temperature 30C⁰), and 99.7% Al₂O₃ ($>1 \times 10^{14}$ Ohms-cm in air at temperature 30C⁰).

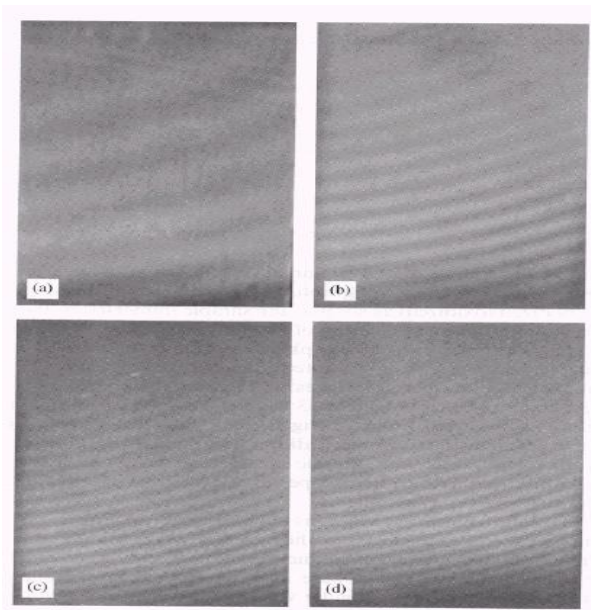


Fig. 2. a,b,c,d progressive interferograms of an aluminium sample anodized in 1.0 % H₂SO₄ solution as a function of time, at (a) 7 fringes at the beginning of the test, at (b) 15 fringes after 2 minutes, at (c) 24 fringes after 5 minutes, at (d) 33 fringes after 8 minutes.

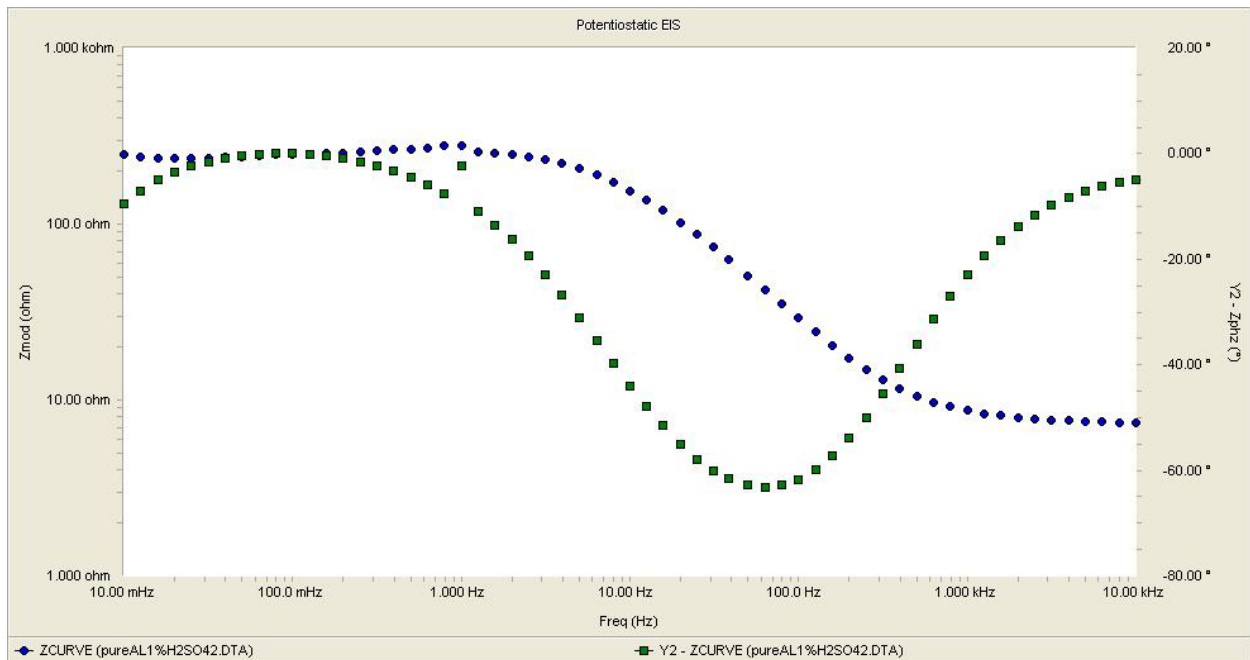


Fig. 3a. Bode plots of the aluminium sample in 1.0 % H₂SO₄.

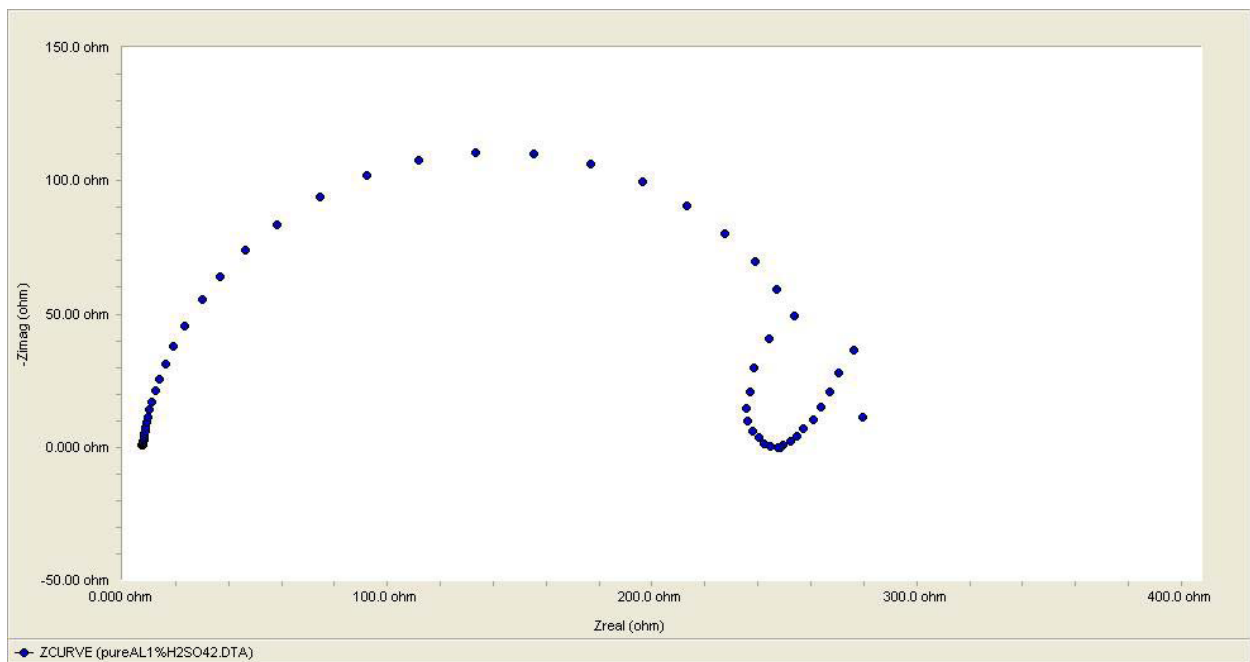


Fig. 3b. Nyquist plot of the aluminium sample in 1.0 % H₂SO₄.

Table 1. Calculated Parameters of Anodized Aluminium samples in different H₂SO₄ concentrations.

Solution Concentration (%H ₂ SO ₄)	AC Impedance x Area(ZA) (Ohms-cm ²)	Total Displacement (U) (µm)	Resistivity By OI (ρ) (Ohms-cm)	Conductivity by OI (σ) (Siemens/ cm)	Resistivity by other source[7] (ρ) (Ohms-cm)
1.0%	5.5x10 ⁶	19.91	2.8x10 ⁹	3.6x10 ⁻¹⁰	5x10 ¹⁰
1.5%	15.0x10 ⁹	21.72	7x10 ¹²	1.43x10 ⁻¹³	5x10 ¹⁰ -1X10 ¹⁴
2.0%	62.5x10 ⁹	42.72	2.5x10 ¹³	4x10 ⁻¹⁴	5x10 ¹⁰ -1X10 ¹⁴
2.5%	5.95x10 ⁹	43.1	1.4 x10 ¹²	7.14x10 ⁻¹³	5x10 ¹⁰ -1X10 ¹⁴

4-References

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