Anodization of Aluminium Samples in Boric Acid Solutions by Optical Interferometry Techniques

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In the present investigation, holographic interferometry was utilized for the first time to monitor in situ the thickness of the oxide film of aluminium samples during anodization processes in boric acid solutions. The anodization process (oxidation) of the aluminium samples was carried out by the technique of the electrochemical impedance spectroscopy(EIS), in different concentrations of boric acid (0.5-5.0% H_3BO_3) at room temperature. In the mean time, the real-time holographic interferometry was used to measure the thickness of anodized (oxide) film of the aluminium samples in solutions. Consequently, holographic interferometry is found very useful for surface finish industries especially for monitoring the early stage of anodization processes of metals, in which the thickness of the anodized film of the aluminium samples can be determined without any physical contact. In addition, measurements of electrochemical values such as the alternating current (A.C) impedance(Z), the double layer capacitance(C_{dl}), and the polarization resistance(Rp) of anodized films of aluminium samples in boric acid solutions were made by the electrochemical impedance spectroscopy(EIS). Attempts to measure electrochemical values of Z, Cdl, and Rp were not possible by holographic interferometry in boric acid especially in low concentrations of the acid. This is because of the high rate of evolutions of interferometric fringes during the anodization process of the aluminium samples in boric acid, which made measurements of Z, Cdl, and Rp are difficult.

Keywords : *holographic interferometry, anodization of aluminium, Al_2O_3 oxide film, alternating current (A.C) impedance, double layer capacitance, polarization resistance, boric acid, aluminium, electrochemical impedance spectroscopy, and he ne laser light.*

1. Introduction

It has been known for some times that the techniques of holographic interferometry are capable of measuring and detecting microscopic changes in a scale less than 1 μm at metallic surfaces in air (1). The techniques are widely accepted because they are non-destructive and a surface alteration of $1/2\lambda$ can be inspected, where λ is the wavelength of the laser light used.

In recent works conducted by the auther,[2]-[6] a novel optical transducer for monitoring the mechanochemical behaviour, i.e. stress corrosion cracking, corrosion fatigue, and hydrogen embrittlement, of metallic electrodes in aqueous solutions has been developed. The optical transducer was developed based on characterization of electromagnetic fields of an object (sample) submereged in aqueous solutions under different conditions of corrosion testings. The characterization of the electromagnetic field of the object was carried out by an optical interferometry technique. The real time-holographic interferometry was applied for recording the intensity and the phase of the electromagnetic field of the object for imaging and data analysis. Also, along with the optical transducer, electrochemical techniques were used for determining various electrochemical parameters of metallic samples in aqueous solutions[2]-[6] In addition, the optical transducer was used to develop an optical corrosion-meter for measuring the corrosion density of metallic alloys under different conditions in non-invassive manners.[7]-[11]

The objective of the present work was to monitor and to measure the thickness of the anodized (oxide) layer of aluminium samples in boric acid solutions by using holographic interferometry. Also, the study aimed to monitor the oxide film during the initiation stage of the anodization phenomenon of the aluminium in different concentrations of boric acid, 0.5-5.0% H_3BO_3. The reason for the selection of aluminium samples in this investigation in, because the aluminium is known to readily anodize

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not only by electrochemical methods but also by only a chemical oxidation reaction.[12] In other words, a thicker oxide layer than the layer which the aluminium normally has in air can form by either electrochemical or chemical methods. Also, by measuring the thickness of the oxide film by holographic interferometry, and the electrochemical parameters, i.e., the A.C.impedance(Z), the double layer capacitance(C_{dl}), and the polarization resistance(Rp) by the electrochemical impedance spectroscopy, of the aluminium samples, one can determine the electrochemical behavior of the anodized film of the aluminium directly without physical contact. This means holographic interferometry can be used as a 3D-interferometric microscope for monitoring the anodization of the aluminium samples during measurements of the Z, C_{dl}, and Rp by the electrochemical impedance spectroscopy.

2. Theoretical analysis

In literature, the relationship between the A.C. Impedance and the double layer capacitance of the anodized film on a metal sample to the thickness of the anodized film on the metal sample is given as the following: [13)-14)]

$$|Z| = 1/C_{dl} = L/(e\ e^\circ\ A) \tag{1}$$

Where: Z: is the A.C. impedance of the oxide film.
  C_{dl}: is the double layer capacitance of the oxide film.
  e: is the dielectric constant, 8.4 of aluminium oxide, Al_2O_3.
  e°: is the permittivity of the free space, 8.85 X 10^{-14} Farad/cm.
  A: is area of the sample.
  L: is thickness of the oxide film which can be obtained by holographic interferometry (Habib, 1993b).

$$L = U = \frac{N\lambda}{(\sin\alpha + \sin\beta)} \tag{2}$$

where: N: is the number of fringes.
  λ: is the wavelength of the laser light used in the experiment.
  $\alpha\&\beta$: are the illumination and the viewing angles, respectively. Both angles can be obtained from the setup of the experiment.

Equation No.1 describes the relationship between the AC. impedance and the double layer capacitance of the oxide film to the thickness of the film. In other words, one can measure the A.C impedance as well as the double

layer capacitance by knowing the thickness of the oxide film. Since the thickness of the oxide film can be measured by holographic interferometry from equation No. 2. Therefore, equation No. 1 can be applied to measure the the A.C impedance as well as the double layer capacitance of the aluminium oxide of aluminium samples during anodization process of the alumnium in boric acid solutions.

Furthermore, in order to relate the electrical resistance of the oxide film on a metal sample to the thickness of the oxide film on the metal sample, the following relationship can be used (15):

$$R = \rho\ L\ /\ A \tag{3}$$

Where: R: is the electrical resistance of the oxide film.
  ρ: is the electrical resistivity of the aluminium oxide film, Al_2O_3, $\rho=10^{16}$ Ohms-cm
  A: is the exposed area of the sample to the solution.
  L: is thickness of the oxide film which can be obtained by holographic interferometry.

Equation No. 3 describes the relationship between the electrical resistance and the thickness of the oxide film. In other words, one can measure the electrical resistance by knowing the thickness of the oxide film. Since the thickness of the oxide film can be measured by holographic interferometry, by using equation No. 2. Therefore, equation No. 3 can be applied to measure the the electrical resistance of the aluminium oxide of aluminium samples during anodization process of the alumnium in boric acid .

3. Experimental work

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 scraches free surface, the samples were etched by a chemical solution for 2 minutes at a temperature ranged between 85-95C^0. 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
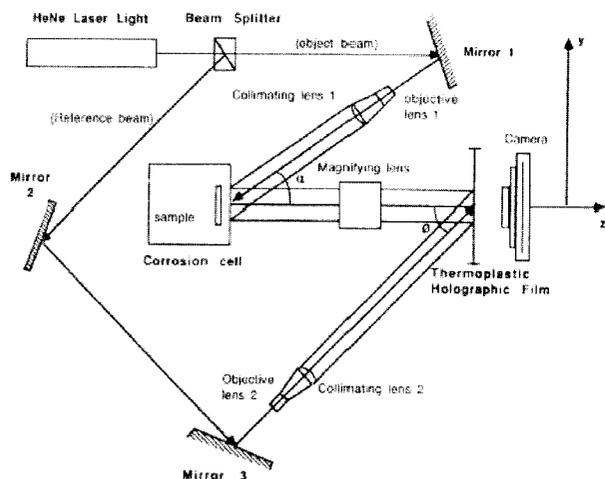
Fig. 1. Optical setup of an off axis holographic interferometry.

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 interferograms of the samples. The camera is HC-300 Thermoplastic Recorder made by Newport Corporation. In the meantime, E.I. specroscopy measurements were conducted using EG&G[16] 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.[16)-17)] During each experiment, the holographic interferograms were recorded as a function of time during the E.I. specroscopy 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 0.5-5 % H_3BO_3 solutions. Furthermore, values of the Z, C_{dl}, and Rp of aluminium samples were measured by the E. I. spectroscopy technique in 0.5-5% H_3BO_3, using Bode,and Nyquist diagrams, respectively.[16)] Also, the obtained interferograms were used to show that a uniform anodization, i.e. oxidation, took place on the aluminium samples during the anodization processes by E.I. spectroscopy measurements.

4. Results and discussion

Fig. 2a,b,c,d,e,f show an example of progressive inter-ferograms of an aluminium sample anodized in 5.0 %
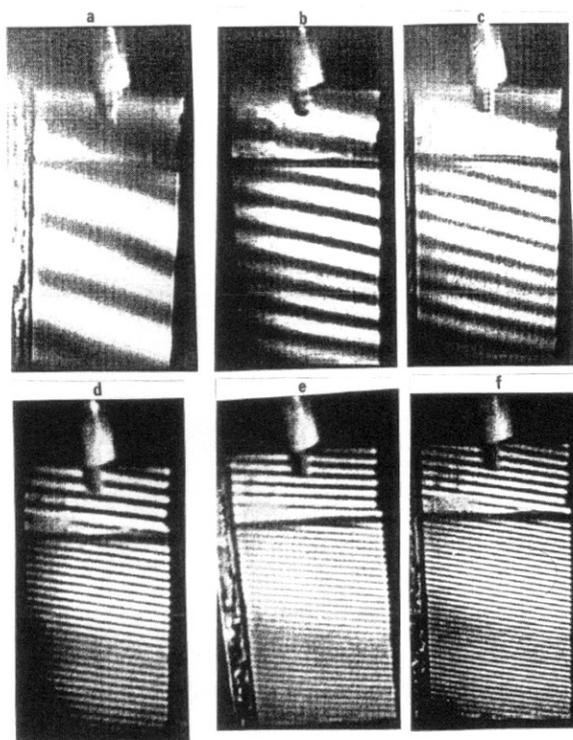

Fig. 2a,b,c,d,e,f shows progressive interferograms of an Aluminium sample anodized in 5.0 % H_3BO_3 solution as a function of time, at (a) 3 fringes at the beginning of the test, at (b) 7 fringes after 3 minutes, at (c) 12 fringes after 6 minutes, at (d) 27 fringes after 11minutes,at (e)31 friges after 13 minutes, at (f) 44 fringes after 17 minutes.

H_3BO_3 solution as a function of time. Fig. 2a represents a real-time interferogram of the sample at the beginning of the test (E.I. spectroscopy measurement), where 3 fringes appeared on the photograph, at f=100 KHz, see Fig. 3a for Bode plot. This indicates that the aluminium sample has rapidly anodized (oxidized) as soon as the sample in immersed in the solution. Fig. 2b is the same interferogram after 3 minutes of elapsed time, where 7 fringes were detected on the photograph, at f=25.1 KHz, see Fig. 3a for Bode plot. It is obvious from this photograph that there is a general chemical oxidation, depicted by the uniform interferometric pattern. Fig. 2c is the same interferogram after 6 minutes, where 12 fringes recorded on the photograph, at f=4 KHz, see Fig. 3a for Bode plot.. Fig. 2d is the same interferogram after 11 minutes, where 27 fringes recorded on the photograph, at f=2.5 Hz, see Fig. 3a for Bode plot. Fig. 2e is the same interferogram after 13 minutes, where 31 fringes recorded on the photograph, at f=1 Hz, see Fig. 3a for Bode plot. Fig. 2f is the same interferogram after 17 minutes, where 44 fringes recorded on the photograph, at f=100 mHz, see Fig. 3a for Bode plot.. It is worth mentioning that each
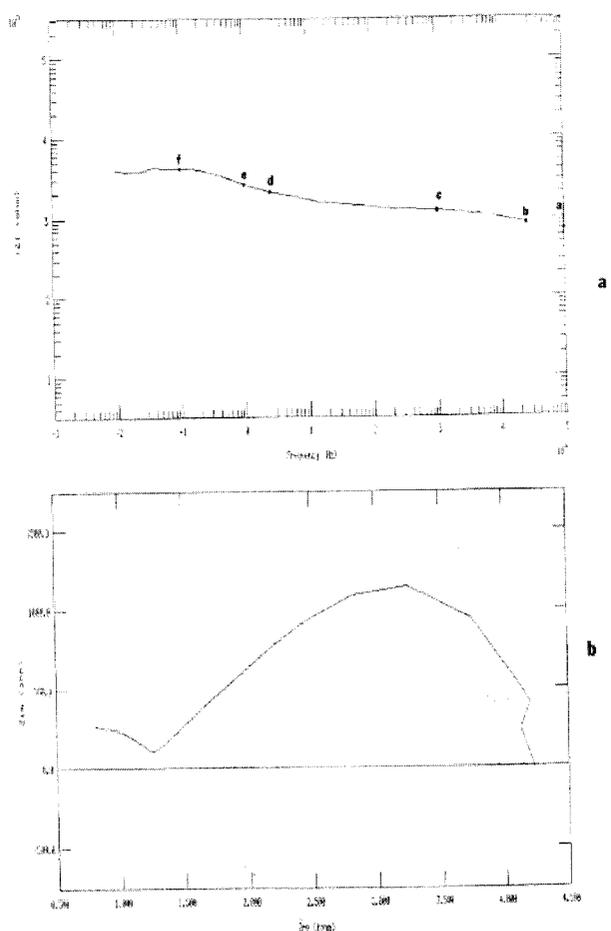
Fig. 3. (a) Bode plot and, (b) Nuquist plot of Aluminium sample in 5.0% H₃BO₃

Table 1. The A.C.impedance, Double Layer-Capacitance, and Polarization resistance values of aluminium samples in different H₃BO₃ concentrations

Solution centration (%H₃BO₃)	No. of fringes (N)	A.C.impedance (f=0.16 Hz) (K Ohms)	Capacitance (f=0.16 Hz) (μ Farad)	Polarization Resistance (KOhms)	E(I=0) (mV)
0.5% (PH=5.85)	N>250	13.5	74.2	32.4	-562
1.0% (PH=5.73)	N>100	12.7	80.1	8.5	-519.5
2.0% (PH=5.13)	50>N>100	11.1	94.6	6.9	-548.5
5.0% (PH=3.7)	N>50	8.7	171.7	4.7	-486.5

fringe in Fig. 2 (dark line) accounts to an orthogonal displacement equivalent to 0.3 μm according to mathematical models reported elsewhere (7and 8). In other words, holographic interferometry can be used as a powerful tool, as a 3D-interferometric microscope, in the field of electrochemistry during different electrochemical measurements.

By using the data from interferograms such as those in Fig. 2, one can develop a retationship between the thickness of the anodized layer (film) and Z, C_{dl}, and Rp, as a function of the elapsed time of the experiment. The Z and Cdl data were determined from Bode plots,[16)-17)] at f=0.16 Hz (at angular velocity =1 rad/sec.), where, W=2 πf, and $C_{dl}=Z^{-1}$. Bode plotes are basically the logarithm of impedance (Z) and phase angle (θ) plotted versus the logarithem of frequency, f, see Fig. 3a for Bode plot of an aluminium sampple in 5.0% H₃BO₃. Values of A.C. impedance and double layer capacitance obtained by electrochemical impedance spectroscopy (E.I.S) are given in Table 1, with respect to the number of fringes observed, N>250, N>100, 100>N>50,and N>50, in 0.5%, 1.0%,

2.0%, and 5.0% H₃BO₃ solutions, respectively.

In addition values of polarization resistance, Rp, obtained by electrochemical impedance spectroscopy(E.I.S) are given in Table 1, with respect to the number of fringes observed, N>250, N>100,100>N>50, and N>50, in 0.5%, 1.0%, 2.0%, and 5.0% H₃BO₃ solutions, respectively. The polarization resistance values were determined from Nyquist plots.[16)-17)] Nuquist plotes are basically the logarithem of the real impedance (Zre) versus the logarithem of the imaginary impedance (Zim), see Fig. 3b for the Nyquist plot of an aluminium sample in 5% H₃BO₃ Solution.

In general, Tables 1 shows that as the acid concentration increases from 0.5-5.0% H₃BO₃, the number of fringes observed to decrease (thickness of the oxide film decreases). In other words, the acid becomes less oxidizing, less active with the aluminium sample, as the concentration of the acid increases. This is clearly shown from the data of the open circuit potential, E(I=0), in which the open circuit potential decreases in the active direction with increasing the acid concentration. In addition, Table 1 shows that as the number of fringes decreases (thickness of the oxide film decreases), values of the Z and Rp increase in a direct proportional manner. This observation is in agreement with the known electrochemical concept[16)-17)] 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. Furthermore, Table 1 shows that as the number of fringes decreases (thickness of the oxide film decreases), values of the double layer capacitance increase in an inversed proportional manner. This behavior correspods well with the predictive behavior of equation No. 4, between the number of fringes and the double layer capacitance.

Attempts to measure electrochemical values of Z, C_{dl},

and Rp were not possible by holographic interferometry in the boric acid solutions, especially in low concentrations of the acid. This is because of the high rate of evolutions of interferometric fringes during the anodization process of the aluminium samples in boric acid, which made measurements of Z, C_{dl}, and Rp are difficult..

5. Conclusions

The following conclusion are drawn from the present investigation:

1. Holographic interferometry was utilized for the first time to monitor in situ the thickness of the oxide film of aluminium samples during anodization processes in boric acid solutions.

2. The anodization process (oxidation) of the aluminium samples was carried out by the technique of the electrochemical impedance spectroscopy(EIS), in different concentrations of boric acid (0.5-5.0% H_3BO_3) at room temperature. In the mean time, the real-time holographic interferometry was used to measure the thickness of anodized (oxide) film of the aluminium samples in solutions.

3. Measurements of electrochemical parameters such as the alternating current (A.C) impedance(Z), the double layer capacitance(C_{dl}), and the polarization resistance(Rp) of anodized films of aluminium samples in boric acid solutions were made by the electrochemical impedance spectroscopy(EIS).

4. Attempts to measure electrochemical values of Z, C_{dl}, and Rp were not possible by holographic interferometry in boric acid especially in low concentrations of the acid. This is because of the high rate of evolutions of interferometric fringes during the anodization process of the aluminium samples in boric acid, which made measurements of Z, C_{dl}, and Rp are difficult.

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