

Structures and Properties of Oxide Barrier-Film of Anodized Aluminum by Electrochemical Impedance Spectroscopy at the Nano-meter Scale

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Abstract

In this study, the effect of the annealing treatment on electrochemical behavior and the oxide barrier-film thickness of anodized aluminum-magnesium (Al-Mg) alloy were investigated. Electrochemical parameters such as the polarization resistance (R_p), solution resistance (R_{sol}), alternating current impedance (Z), and the double layer capacitance (C_{dl}) of the anodized Al-Mg alloy were determined in sulfuric acid solutions ranged from -1 % H_2SO_4 by electrochemical impedance spectroscopy (EIS) methods. Then, the oxide film thickness of the anodized Al-Mg alloy was determined from the obtained electrochemical parameters as a function of the sulfuric acid concentration (-1 % H_2SO_4), in the as received sample and annealed sample conditions. The optimum thickness of the oxide film was determined for the as received samples (4.2nm) and for the annealed samples (0.63nm) in sulfuric acid concentrations of 4% and 2% H_2SO_4 , respectively. The reason behind the oxide film thickness of the as received samples is greater than the one for the annealed samples, because the former samples are thermodynamically unstable (more chemically active) as compared to the annealed samples. A mathematical model was developed to interpret the mechanism of the oxide film build up on the aluminum substrate. The mathematical model of the oxide film build up on the aluminum substrate was proposed for the next challenge of the present work.

Keywords: Intermetallics; Surface treatments; Anodized Al-Mg alloy; Thin films; Electrochemical impedance spectroscopy (EIS); and Electrical properties.

Introduction

It has been known that the formation of anodic oxide films is a common means of achieving corrosion protection of aluminium and its alloys. For example, the formation of a porous oxide layer, with an underlying barrier (compact) oxide film, is normally achieved in acidic media [1], while barrier (compact) oxide films alone are typically formed in neutral buffer solutions [2]. The porous oxide layers are preferred to the barrier (compact) films because they can form to high oxide thickness and yield excellent abrasion protection. Also, the porous oxide layers provide improved corrosion resistance after chemically sealing of the pores. There is a number of methods for the determination of the oxide film thickness and among those methods are the optical interferometry [1] and the Electrochemical Impedance Spectroscopy (EIS) [2]. The optical interferometry is found very useful of determining the porous oxide-layer thickness of anodized aluminum alloy in a micrometer scale. On the other hand, the Electrochemical Impedance Spectroscopy (EIS) is found very useful technique of determining the oxide barrier-film thickness of anodized aluminum alloy in a nano-meter scale [2]. A detail discussion of both methods are given elsewhere [1,2]. Also, the discussion includes some examples of the determination of the oxide film layer by optical interference and electrochemical impedance spectroscopy (EIS).

In general, the EIS is an alternating current (A.C) method for corrosion studies of metallic, organic, and inter-metallic samples in relatively high resistive conditions. For instance, high resistive solutions, inhibited solutions, organic coated samples, high resistive-oxide forming samples, like in the present case, are considered high resistive conditions. The reason one would use the EIS rather than direct current (D.C) methods for corrosion studies of samples in such high resistive conditions is to avoid erroneous results due to heating of samples in the D.C method in such conditions [3,4]. Normally the results of the EIS consist of two plots. The first plot is the complex plane plot (Nyquist Plots) which is basically the logarithm of the imaginary

impedance (Z_{image}) versus the logarithm of the real impedance (Z_{real}). The values of the polarization resistance (R_p) and the solution resistance (R_s) can be obtained by the data fitting method of the Randell's semi circle [3,4]. The second plot is the Bode plot which is basically the logarithm of impedance (Z) (Y-coordinate) and the phase (θ) (Y-coordinate) plotted versus the logarithm of the frequency (X-coordinate). Values of the alternating current (A.C) impedance and the double layer capacitance can be obtained from the Bode plot at a low frequency based on the extrapolation of the intersection line at a frequency equal to 0.16 Hz from the x-coordinate in Bode plots, to the y-coordinate in Bode plot.

The objective of this study was to determine the oxide barrier (compact)-film thickness and the electrochemical parameters of anodized aluminium-magnesium (Al-Mg) alloy by A.C techniques. Electrochemical parameters such as the polarization resistance, solution resistance, alternating current (A.C) impedance, and the double layer capacitance of the anodized Al-Mg alloy were determined in sulfuric acid solutions (-1 % H_2SO_4) by electrochemical impedance spectroscopy (EIS) methods. Then, the oxide barrier- film thickness of the anodized Al-Mg alloy was determined from the obtained electrochemical parameters as a function of sulfuric acid concentration (-1 % H_2SO_4) by applying the following relationship [3]:

$$C_{dl} = 1/Z = (e e A/L) \quad (1)$$

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Where

C_{dl} is the double layer capacitance of the oxide film

Z is the alternating current (A.C) impedance of the oxide film

ϵ is the dielectric constant, 8.4 of the aluminum oxide, Al_2O_3 ,

ϵ_0 is the permittivity of the free space, 8.85×10^{-14} F/cm

A is the exposed surface area of the sample to the aqueous solution

L is the oxide Barrier- film thickness.

Therefore, from Equation No.1, one can determine the oxide barrier- film thickness from the obtained electrochemical parameters, i.e., the double layer capacitance of the oxide film, as the following [3]:

$$L = (\epsilon \epsilon_0 A / C_{dl}) \quad (2)$$

Equation No.2 will be used in this study to determine the oxide film thickness of the Al-Mg alloy as a function of sulfuric acid concentration (-1 % H_2SO_4).

Experimental Works

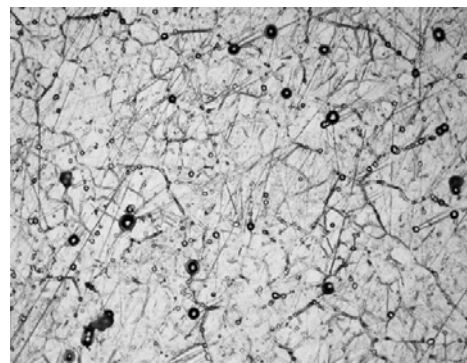
In the present investigation, an Aluminum-Magnesium (Al-Mg) alloy was used. The alloy composition comprises of 0.27% Fe, 1.7%Mg, and balanced aluminum, known to be 636 Aluminium alloy. The samples were fabricated in a cylindrical form with a diameter of 2cm, for the electrochemical investigation, according to the standard methods of the American Society for Testing and Materials [4]. Then, some of the samples were solution annealed at 45°C for two hours in an electric furnace, then, the samples were slow cooled in the furnace. Thereafter, all samples (annealed and as received samples) were polished and ground by silicon carbide papers until the finest grade (12) was reached. Then, a set of the annealed and the as received samples were prepared for metallographic examinations, in order to determine the microstructures of the samples. An optical light microscope (Made by Nacet, France) was used for the metallographic examinations.

For determination of the electrochemical parameters of the annealed and the as received samples, all EIS measurements were performed against a saturated calomel electrode (SCE) according to procedures described elsewhere [4]. A standard electrochemical cell was used, the cell made of a 1 cm³ flask, a reference electrode, the saturated Colomel electrode (SCE), a counter electrode, made of platinum wire, and a working electrode, annealed and as received Al-Mg Samples. The exposed surface area of all samples was 3.14 cm². In this study, EIS measurements were conducted using a potentiostat/Galvanostat made by Gamry instruments in order to obtain impedance spectra. The EIS spectra of the annealed and as received samples of Al-Mg alloy were determined in, 2,4,6,8,1 % H_2SO_4 . The sulfuric acid solution was diluted by distilled water. Values of the polarization resistance and the solution resistance were obtained by the complex plane plots (Nyquist plots). The complex plane plots (Nyquist Plots) are basically the logarithm of the imaginary impedance (Z_{image}) versus the logarithm of the real impedance (Z_{real}). The values of the polarization resistance (R_p) and the solution resistance (R_s) were obtained by the data fitting method of the Randell's semi circle. Also, values of the alternating current (A.C) impedance and the double layer capacitance were obtained from Bode plots at a low frequency. The alternating current (A.C) impedance and the double layer capacitance were obtained at low frequency based on the extrapolation of the intersection line at a frequency equal to 0.16 Hz from the x-coordinate in Bode plots, to the y-coordinate in Bode plot.

Bode plots are basically the logarithm of impedance (Z) (Y-coordinate) and the phase (θ) (Y- coordinate) plotted versus the logarithm of the frequency (X-coordinate). All the electrochemical parameters of the Al-Mg samples were determined by using Gamry's based software. It is worth noting that there was no delay time at the beginning of each test during the measurements of the electrochemical parameters of the Al-Mg samples in, 2, 4, 6, 8, 1 % H_2SO_4 . This step was necessary to avoid any chemical oxidation of the samples. Also, in order to plot the complex plane (Nyquist) and Bode plots, the frequency range was chosen to range between 1Hz to .1Hz. Finally the obtained data of the alternating current (A.C) impedance and the double layer capacitance, of all investigated samples, were used to measure the oxide film thickness of by using equation No. 2, as a function of the sulfuric acid concentration, 2,4,6,8,1% H_2SO_4 .

Results and Discussion

Figures 1 and Figure 2 show the microstructures of the Al-Mg alloy in the as received and annealed conditions, respectively. It is obvious from Figure 1 and Figure 2 that the microstructures of the Al-Mg samples in the as received and annealed conditions consists of two distinguished phases. The matrix phase is (Al) phase, white phase. In contrast, the second phase is in a form of second phase particles, β phase (Al_3Mg_2), dark phase. The different between the microstructures of the as received sample (Figure 1) and the annealed sample (Figure 2) are



1 μ m

Figure 1: shows the microstructure of the Al-Mg alloy in the as received condition. The magnification of the figure is 2 X, of an average grain size of 1 μ m of the (Al) Phase.

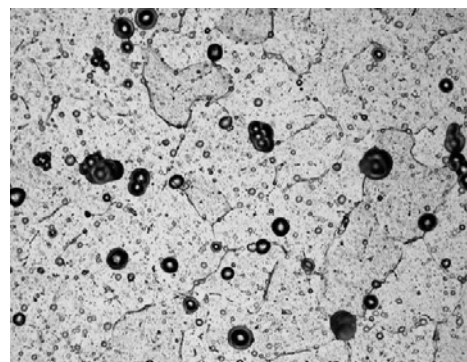


Figure 2: shows the microstructure of the Al-Mg alloy in the annealed condition. The magnification of the figure is 2 X, of an average grain size of 224 μ m of the (Al) Phase.

in the grain size of the (Al) phase as well as the size of the second phase particle, the β phase. It is clear that the average grain size of the (Al) Phase is larger in the annealed sample than in the as received condition. The average grain size of the (Al) Phase is found equivalent to 224 μm as compared to 1 μm for the as received sample. The average grain size has been determined by the line intersection method according to the standards of the American Society of Metals [5]. In addition, the second phase particle (β phase) is found larger and coarser in the annealed sample than in the as received sample. This occurred because the annealed sample was normalized (slow cooled in the furnace) after the solution annealing treatment for two hours at 45°C in an electric furnace. As a result this led to the precipitation of the second phase particles (β phase), by nucleation and growth, in the (Al) matrix phase. Then second phase particles were enlarged by coalescing with other second phase particles, see (Figure 2). This process eventually led to the coarsening of the second phase particles when the temperature of the furnace reached the room temperature.

The oxide film thickness of the as received samples was obtained by using Equation No.2, and using the obtained values of the double layer capacitance. The obtained data in Table 1 show that as the concentration of the sulfuric acid increased from -4% H_2SO_4 , the polarization resistance and the double layer capacitance decreased from 12.22 to 0.6 Kohms and 31.3 to 5.61 μF respectively.

In contrast, as the concentration of the sulfuric acid increased from -4% H_2SO_4 , values of the alternating current impedance and the oxide film thickness were observed to increase from 31.95 to 178K ohms and 0.75 to 4.2 nm, respectively. This observation is in agreement with the known electrochemical concept 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 [3]. Consequently, the values of the double layer capacitance decreased because the double layer capacitance has an inverse proportional relationship with the alternating current impedance, see Equation No1. In the meantime, the polarization resistance was observed to decrease from 12.22 to .6K ohms because of the high tendency of the Al element, in general, to oxidation (anodization) in sulfuric acid solution. On the contrary, the solution resistance was observed to decrease all the way from 1.3K ohms to .65 ohms as the solution concentration increased from 1% H_2SO_4 . This naturally occurred because of increase of the density of the ionic species in the distilled water. In other words, the addition of sulfuric acid from -1 % H_2SO_4 to the distilled water has increased the distilled water conductivity. Furthermore, the obtained data in Table 1, show that as the concentration of the sulfuric acid increased from 4-1 % H_2SO_4 , the polarization resistance was observed to increase first from 0.6 to 2.58K ohms, then decrease to 0.45K ohms. On the other hand, the double layer capacitance was observed to increase from 5.61 to 29.61 μF as a function of the increase of the sulfuric acid concentration from 4-1% H_2SO_4 . In contrast, as the concentration of the sulfuric acid increased from 4-1 % H_2SO_4 , values of the alternating current impedance and the oxide film thickness were observed to decrease from 178 to 33.8K ohms and 4.2 to 0.8 nm, respectively. This observation is in agreement with the known electrochemical concept of as the thickness of the oxide layer decreases, the resistance (impedance) of the metal decreases as well, because the oxide film becomes less protective of the base metal from the surrounding environment. Consequently, the value of the double layer capacitance was observed to increase because the double layer capacitance has an inverse proportional relationship with the alternating current impedance. In addition, Figure 5 shows the Nyquist plots of the annealed samples of Al-Mg alloy in the, 2,4,6,8,1 % H_2SO_4 .

From the Nyquist plots the polarization resistance, solution resistance, alternating current (A.C) impedance, and the double layer capacitance of the Al-Mg alloy were determined in the annealed conditions in, 2, 4, 6, 8, 1 % H_2SO_4 .

Tabulated values of the polarization resistance, solution resistance, alternating current (A.C) impedance, the double layer capacitance, and the oxide film thickness of the annealed samples of the Al-Mg alloy are given in Table 2.

In the same way, the oxide film thickness of the annealed samples was measured by implementing Equation No.2, and using the obtained values of the double layer capacitance. From the obtained data in Table 2, one can tell that as the concentration of the sulfuric acid increased from -1 % H_2SO_4 , values of the polarization resistance and the solution resistance were observed to decrease from 14.71K ohms and 3.36K ohms to a steady state value of .1K ohms and .1K ohms, respectively. In contrast, as the concentration of the sulfuric acid increased from -1 % H_2SO_4 , values of the alternating current impedance and the oxide film thickness were observed to increase first from 24.15 to 26.93K ohms and 0.56 to 0.63 nm, respectively. Then, the values of the alternating current impedance and the oxide film thickness were observed to attain a steady state value of around 17K ohms and 0.4 nm, respectively. The electrochemical behavior of the annealed samples was expected to behave as the as received samples as a function of the sulfuric acid concentration.

In contrast, the double layer capacitance was observed to vary several times in a range between 37.1 3 to 62.18 μF as a function of the increase of the sulfuric acid concentration from -1% H_2SO_4 . This behavior was unexpected ,because the double layer capacitance should have an inversely proportional relationship with the alternating current impedance. In order to obtain the optimum thickness of the oxide film with respect to the sulfuric acid concentration, plots of the oxide film thickness versus the sulfuric acid concentration were constructed.

Figure 6 shows the relationship between the oxide film thickness and the sulfuric acid concentration, for the as received and annealed samples, of the Al-Mg alloy. The figure show clearly at sulfuric acid concentrations of 4% and 2% H_2SO_4 , the optimum thickness of the oxide film was determined for the as received samples (4.2nm) and for the annealed samples (0.63nm), respectively. The reason behind

% H_2SO_4	R_p (Kohms)	R_s (Kohms)	C_{dl} (μF)	Z (Kohms)	L (nm)
	12.22	1.3	31.3	31.95	.75
2	1.72	.623	9.36	17	2.5
4	.6	.52	5.61	178	4.2
6	1.53	.57	8.8	124	2.9
8	2.58	.53	8.4	119	2.8
1	.45	.65	29.61	33.8	.8

Table 1: The Electrochemical Parameters and the Oxide Film thickness of Al-Mg alloy in the as Received Condition in Different H_2SO_4 Concentrations.

% H_2SO_4	R_p (Kohms)	R_s (Kohms)	C_{dl} (μF)	Z (Kohms)	L (nm)
	14.71	3.36	41.4	24.15	.56
2	.2	.26	37.13	26.93	.63
4	.11	.12	62.18	16.1	.375
6	.14	.11	53.9	18.83	.44
8	.11	.3	59.13	16.91	.395
1	.885	.63	5.4	19.84	.463

Table 2: The Electrochemical Parameters and the Oxide Film thickness of Al-Mg alloy in the annealed Condition in Different H_2SO_4 Concentrations.

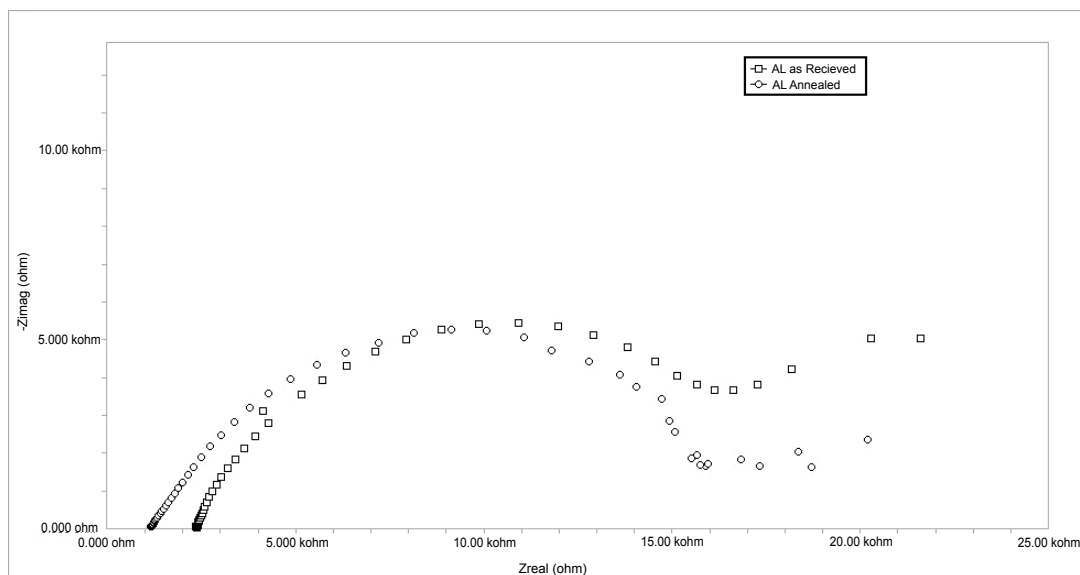


Figure 3: Shows the Nyquist plot of the as received and annealed samples of Al-Mg alloy in % H₂SO₄.

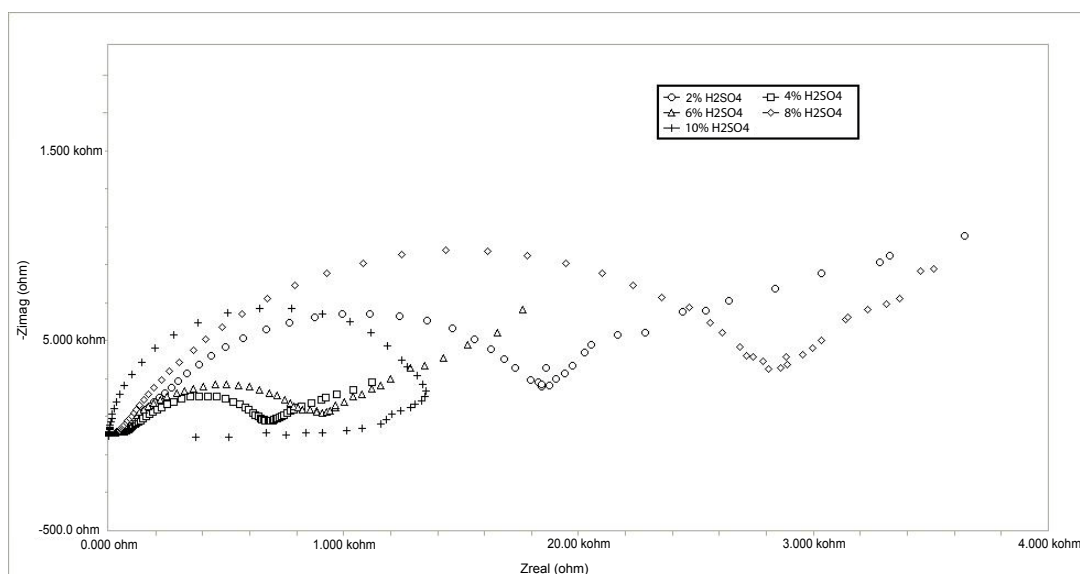


Figure 4: Shows the Nyquist plot of the as received samples of Al-Mg alloy in 2%-10 % H₂SO₄.

the oxide film thickness of the as received samples is greater than the one for the annealed samples, because the former samples are thermodynamically unstable (more chemically active) as compared to the annealed samples. In addition, this observation is in agreement with the fact that the E.I. Spectroscopy is useful technique to determine the electrochemical parameters and the oxide barrier (compact)-film thickness of aluminum alloys [2].

Mathematical model of the oxide film build up on the aluminum substrate

In order to develop a general model of the mechanism of the oxide barrier-film build up on the aluminum substrate during the anodization of the aluminum, one should consider the following:

1-The aluminum substrate always has a thin oxide film, due to the oxidation of aluminum in air.

2-The aluminum half reaction is as the followings:



during the anodization of the aluminum in an electrochemical cell made of aluminium electrode/sulfuric acid solution .

3-The oxidation of the aluminum substrate in equation 3 and equation 4 is governed by the applied electrochemical potential (E), described by Nernst's equation 6 as the following:

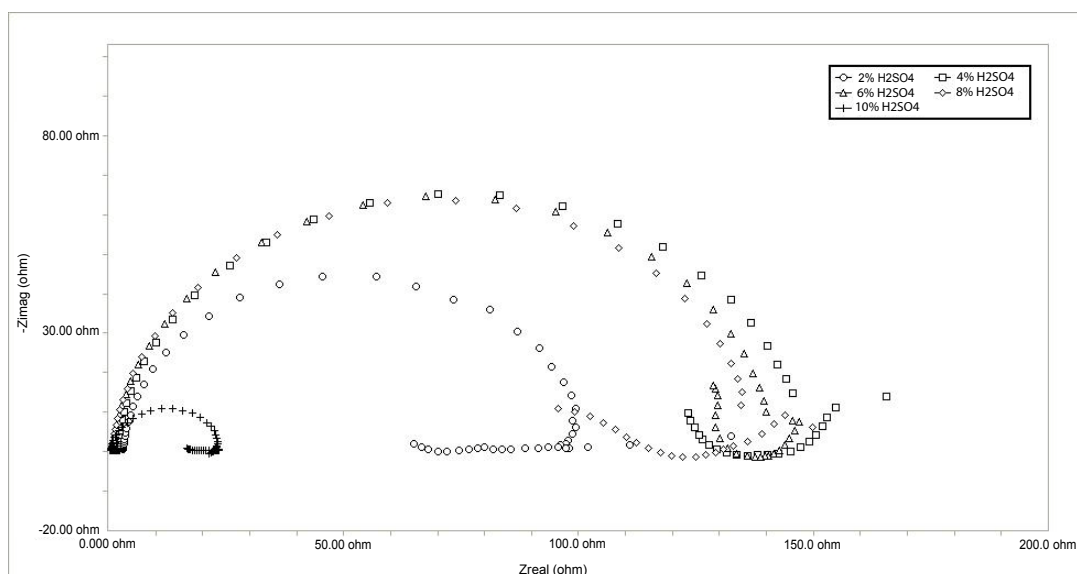


Figure 5: Shows the Nyquist plot of the annealed samples of Al-Mg alloy in 2%-1 % H₂SO₄.

$$E = E^{\circ} + [RT/nF] \ln[(Al^{+3})/(Al)] \quad (6)$$

Where

E^o is the equilibrium potential.

R is the ideal gas constant.

T is the absolute temperature of the solution.

n is the electronic charge number.

F is Faraday 's constant.

(Al⁺³) is the concentration of Al⁺³.

(Al) is the concentration of Al.

4-Finally, the mathematical model is not only a function of the electrochemical potential (E) of the oxidation of aluminum substrate, described in equation 3 and equation 4, but also, the mathematical model is a function of a number of independent variables. The mathematical model is a function of the Oxygen transport in the oxide barrier -film above the aluminum substrate, a function of the Oxygen diffusion through the porous oxide- layer above the in the oxide barrier-film, and a function of time. In other words, the mathematical model is a function of Oxygen diffusion flux (N_s), solid diffusion, in the oxide barrier (compact)- film , a function of the Oxygen flux through the porous Oxide layer (N_p),porous diffusion, and time(t). So, the general form of the model is derived as the following:

$$L = L(E, N_s, N_p, t) \quad (7)$$

L is the oxide barrier-film thickness.

E is the applied electrochemical potential, see in Equation.6.

N_s is the Oxygen flux in oxide barrier-film.

N_p is the Oxygen flux in the porous oxide layer and N_p is equal to the following:

$$N_p = N_v + N_d \quad (8)$$

Where

N_v is the Oxygen viscous flux in the pores.

N_d is the Oxygen diffusion flux in the pores.

So, the supply of Oxygen to the aluminum substrate, as described in equation.5, is actually consists of

$$N_s + N_p = N_s + N_v + N_d = \quad (9)$$

and details of the derivation of equ. 9 are given elsewhere [7&8] as the followings:

First by letting, N_s + N_p = N_s + N_v + N_d = N_i^{7&8}, where

$$N_i = -\frac{1}{RT} \left[K_0 S_1 + \frac{B_0 P}{\mu_1} + Q e^s \right] \frac{dP}{dL} \quad (10)$$

N_i indicating that the Oxygen is the single component (O₂=1) flowing through the oxide barrier (compact)- film and through the porous Oxide layer.

Where

R is the ideal gas constant.

T is the temperature of the solution.

K₀ is defined as a structural parameter which is equal to:

$$\frac{2}{3} a X \left(\frac{\epsilon^G}{\tau^G} \right) \quad (11)$$

Where "a" is the pore radius and ε^G is the void fraction and τ^G is the tortosity factor; which is equal to the inverse of the void fraction if not known [7]. The superscript G denotes the gas phase.

The unit on K₀ is centimeters (cm). S₁ is the velocity of gas molecules defined as:

$$S_1 = \left(\frac{8RT}{\pi M_R} \right)^{\frac{1}{2}} \quad (12)$$

Where M_R is the molecular weight of the Oxygen, (R=O₂), in flux (O₂ = 3.2 x 1⁻² kg/mol; This first term (K₀S₁) therefore represents the contribution of the diffusive porous flux, in which a > τ^G.

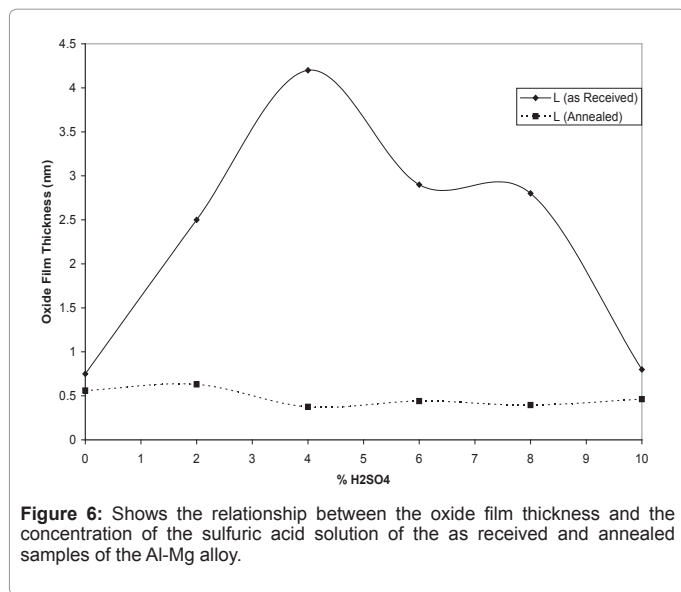


Figure 6: Shows the relationship between the oxide film thickness and the concentration of the sulfuric acid solution of the as received and annealed samples of the Al-Mg alloy.

P is the pressure (units: mmHg \rightarrow 1333.2 g/cm²s²) and μ_1 is the Oxygen viscosity

B_0 is the structural parameter defined as:

$$\frac{1}{8} a^2 \times \left(\frac{\epsilon^G}{\tau^G} \right) \quad (13)$$

This term, $\frac{B_0 P}{\mu_1}$ therefore is the contribution of the viscous flux through the pore, in which $a < \tau^G$.

Additionally $Q_1 e^s$ is the "effective" gas (Oxygen) permeability in the aluminum oxide.

This term thereby represents the solid flux of gas through the oxide barrier- film. The differential $\frac{dP}{dL}$ is the pressure gradient imposed by the system, if that existed during the anodization of the aluminum substrate.

Assuming if the pressure existed during the anodization of the aluminum substrate, then the boundary condition would be of such that at, the oxide barrier- film thickness, $L = 0$ then $P = P(0)$ and when $L = l$ then $P = P(l)$ where l is a nanometer scale. This then leads to the following simplification:

$$\Delta P = P(0) - P(l).$$

Furthermore another simplification can be made:

$$P_{average} = \frac{p(0) - p(l)}{2} \quad (14)$$

Therefore when integrating the N_1 equation leads to the following equation:

$$N_1 = -\frac{1}{RT} \int_0^l \left[K_0 S_1 + \frac{B_0 P}{\mu_1} + Q_1 e^s \right] \frac{dP}{dL} \quad (15)$$

The above mathematical model, equation 7, was given only to describe the mechanism of the processes of the buildup of the oxide barrier- film on the aluminum substrate. The mathematical model will not be used to predict the processes of the buildup of the oxide film on the aluminum substrate by solving the model, using empirical data, because such empirical data are very difficult to obtain on the aluminum/oxide barrier (compact)-film/porous oxide-layer

structure. The solution of equation 7 will be the next challenge of the present work.

Conclusions

The following conclusions are drawn from the present investigation:

The thickness of the oxide film was determined based on the obtained electrochemical parameters by EIS, see Tables 1 and 2 for both conditions. The optimum thickness of the oxide film was detected for the as received samples (4.2nm) and for the annealed samples (0.63nm) in sulfuric acid concentrations of 4% and 2% H₂SO₄, respectively. The reason behind the oxide film thickness of the as received samples is greater than the one for the annealed samples, because the former samples are thermodynamically unstable (more chemically active) as compared to the annealed samples. Consequently, The E.I. Spectroscopy is found useful technique to determine the electrochemical parameters and the oxide barrier (compact)-film thickness of aluminum alloys. In addition, a mathematical model of the oxide film build up on the aluminum substrate was proposed for the next challenge of the present work.

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