Coloring the Layer Thickness of Anodized Aluminum by Integral Color Process

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ABSTRACT

The identification of the self coloring process in anodizing process is integral color. In this research specimens of pure aluminum (1000) and AA 5056 anodized by using Alternative Current (A.C) techniques were investigated under standard conditions and electrolytically colored in sulfuric acid baths solutions at different operating conditions [Alternative Current density (A.C) (2-3) Amp/dm^2, electrolyte concentration (2-6) Normality, electrolyte temperature (15-25) C^o and anodizing time (20-60) minutes]. The experimental work was designed according to (Box-Wilson) method by using second order polynomial model between four variables and thickness of anodic layer for the two types of materials and substituted the experimental results for anodizing process in proposed model to calculate the coefficients of the mathematical equations to find an expression for obtaining best film thickness. The coloring deposition efficiency increases with the increase of applied electrolytic coloring alternative current and the purity of aluminum.

Under standard electrolytic coloring conditions, the current efficiency for coloring deposition is low for all examined materials. However, pure aluminum has much higher coloring deposition efficiency than the alloy. The anodizing alternative current density affects the electrolytic coloring process to a lesser degree for alloy than for pure aluminum, indicating the role of the morphology of the oxide film. The increases of anodizing temperature and porous layer thickness have marginal effect on electrolytic coloring process. Understanding the effect of alloy types on electrolytic coloring process will enable us to achieve color uniformity and to expand color and shade selections.

Keywords: Coloring Aluminum, Integral color, AC Coloring Process, Anodizing.

تلوين سمك طبقة الالمنيوم الموأنود بعملية التلوين التكاملية

الخلاصة

تعرف عملية التلوين الذاتي في عملية الانودة بالتلوين التكاملي. في هذا البحث تم فحص واختبار نماذج من سبيكة الالمنيوم النقية (١٠٠٠) وسبيكة غير نقية (٥٠٥٦) في عملية الانودة تحت ظروف قياسية وتلوينها الكتروليتيا في محلول حامض الكبريتيك في ظروف تشغيل مختلفة

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(كثافة التيار الكهربائي المتناوب ٢-٣ امبير/دسم٢, تركيز المحلول الالكتروليتي ٢-٦ عيارية, درجة حرارة المحلول ١٥-٢٥ مئوي وزمن الانودة ٢٠-٦٠ دقيقة. التجارب العملية صممت حسب طريقة البوكس ولسن باستخدام معادلة من الدرجة الثانية بين المتغيرات الاربعة وسمك طبقة الانودة لكلا السبيكتين وتم تعويض النتائج العملية لعملية الانودة في الموديل الرياضي المقترح لحساب توابت المعادلة الرياضية وعرفت بالمعادلة المعبرة للحصول على اعلى سمك من طبقة اوكسيد الالمنيوم. كفاءة ترسيب اللون ازدادت مع زيادة كثافة التيار الكهربائي المتناوب ومع نقاوةالالمنيوم.
تحت ظروف التلوين الالكتروليتية, كفاءة الترسيب اللوني منخفضة لكل النماذج. سبيكة الالمنيوم النقية كانت الاكثر بالترسيب اللوني من السبيكة الغير نقية. ان تاثير كثافة التيار الكهربائي المتناوب في عملية التلوين الالكتروليتي لسبيكة الالمنيوم الغير نقية اقل مما هو لسبيكة الالمنيوم النقية, نسبة الى تركيب طبقة الاوكسيد. ان الزيادة في درجة الحرارة ومسامات سمك طبقة الانودة له تاثير هامشي في عملية التلوين الالكتروليتية. تم الاستنتاج بان تأثير نوع السبيكة في عملية التلوين الالكتروليتية سوف تمكننا من انجاز لون موحد وان نتوسع في تدرجات الالوان.

INTRODUCTION

Various methods for coloring anodized aluminum have been developed [1–3]. One of the most widely used coloring methods for the past decades is electrolytic coloring. During this process, aluminum is first anodized in sulfuric acid solution, followed by an alternating current electrolytic deposition of a metal (tin, nickel, cobalt, etc.) at the base of the pores of the anodic coating[4–6]. Integral color anodizing is generally done with organic acids, but the same effect has been produced in laboratory with very dilute sulfuric acid electrolyte and a pulsed current [6]. The anodized aluminum oxide layer consists of open pores that can be impregnated with coloring pigments to provide colors. The anodized coating can be colored by dye or electrolytic coloring method. Dyeing coloring agents can be organic or inorganic, achieving nearly limitless color options. Organic dyes, however, are not resistant to UV light and are more suitable for indoor applications. Electrolytic coloring uses an a.c. current to deposit metal into the pores; it is color-fast and has many industrial applications [8–9].

Valuable works on the behavior of several intermetallic compounds during anodizing were carried out about 60 years ago by Keller et al. and by Fischer et al [10]. About 30 years ago Spooner, Brace and other researchers (Alcan Laboratories) [10] tried to establish the electrochemical reactivity of several alloying elements and the behavior of several intermetallic compounds in aluminum alloys during sulfuric acid anodizing under constant voltage. In the meantime the anodic oxidation of aluminum alloys was extensively investigated [11, 12]. Attention was given primarily to the oxidation of alloying elements at the alloy/film interface during the formation of barrier type anodic films. However, the findings are also considered to be applicable to the formation of porous anodic films. The influence of the AC coloring voltage, composition and pH of the coloring bath, as well as the anodizing conditions on the electrolytic coloring process have been studied [13–20]. However, the effects of various alloying elements on the electrolytic coloring of anodized aluminum alloys have not been extensively investigated.

The purpose of this research was to investigate the effect of different operating conditions [Alternative Current density (A.C) (2-3) Amp/dm^2, electrolyte

concentration (2-6) Normality, electrolyte temperature (15-25) C^o and anodizing time (20-60) minutes] and alloy types in the sulfuric acid anodizing process on the electrolytic coloring process were investigated. Specimens of the pure aluminum 1000 and AA 5056 anodized under different conditions were compared with those of pure aluminum during the electrolytic coloring at standard conditions.

EXPERIMENTAL DESIGN

The proper technique for planning a system of more than three variables "central composite rotatable design" the total number of treatment combination is equal to (2^K +2K+1), where (K) is the number of variables, plus additional further treatments to take the lack of fit and experimental error in to account. These designs consists of a 2^K fractional (i.e. coded to the usual ± 1 notation) augmented by 2K axial points [i.e (± ,0,0,…..,0),(0, ±, 0,…..,0), (0,0, ±,…..,0), …., (0,0,…., ±,) and center points (0,0,0,…..,0)].

A preliminary step is to set up the relationships between the coded levels and the corresponding real variables, these relationships are as follows [20, 21]:

$$X_{Coded} = \frac{[X_{actual} - X_{center}]}{\left[\frac{X_{center} - X_{\min.}}{\sqrt{K}}\right]} \quad \ldots (1)$$

The experimental work was designed in the following experimental ranges:-

1. Alternative Current density ranged from 2 to 3 Amp. /dm^2.
2. Concentration of the electrolytic solution (H_2SO_4) ranged from 2 to 6 N.
3. Operation temperature ranged from 15 to 25 C^o.
4. Anodizing time ranged from 20 to 60 min.

The central composite rotatable design of four variables was used. The coded levels were related to real process values of these variables as follows:

$$X_1 = \frac{A-2.5}{0.25} \quad \ldots (2)$$

$$X_2 = \frac{C-4}{1} \quad \ldots (3)$$

$$X_3 = \frac{T-20}{2.5} \quad \ldots (4)$$

$$X_4 = \frac{t-40}{10} \quad \ldots (5)$$

Where: A is the Alternative Current density in (Amp. /dm^2), C is the concentration of electrolytic (H_2SO_4) solution in normality (equiv. /liter), T is the operating temperature in (C^o) and t is time of anodizing in min.

The workings ranges of coded and corresponding real variables are listed in Table (1) Thirty one experiments were carried out in a sequence shown in Table (2)

where the coded values +2, -2, 0 present the maximum, minimum and average values respectively.

The polynomial equations for a system of four variables can be represented as follows:

$$Y=B_0+B_1X_1+B_2X_2+B_3X_3+B_4X_4+B_{11}X_1^2+B_{22}X^2_2+B_{33}X^2_3+B_{44}X^2_4+B_{12}X_1X_2+B_{13}X_1X_3 + B_{14}X_1X_4+B_{23}X_2X_3+B_{24}X_2X_4+B_{34}X_3X_4. \quad \ldots\textbf{(6)}$$

Where: Y is the Objective function (film thickness).

The corresponding coefficients of the above polynomials are called "The Regression Coefficients".

EXPERIMENTAL WORK

A series of specimens that conducting sulfuric acid anodizing were prepared to study the effect of the most affective variables (i.e current density, concentration of electrolyte , temperature and time) on anodizing of pure aluminum alloy (1000) and aluminum – magnesium alloy (5056). These variables had been correlated with the thickness of the specimen by a second order polynomial model after estimation of the coefficients would carry over according to one of the methods of optimization.

The present study includes the achievement of experiment work through central composite rotatable designed method to create specimens of different artificial film thickness using sulfuric acid anodizing process. The operating conditions using sulfuric acid anodizing process were commenced with alternative current density in the range 2-3 Amp./dm^2, sulfuric acid concentration in the range 2-6 N, temperature of electrolyte in the range 10-25 C^o, and time of exposure in the range 20-60 min. Table (3) listed chemical composition of the alloy according to UK or USA specification [22,23]. The chemical composition for the material According to the Analysis of (Central Organization for Standardization and Quality Control) was listed in Table (4).

MATERIALS AND METHODS

The studied material was supplied in a sheet form of 3 mm thickness. The sheet is cut into specimens with dimensions about (100*45*4) mm of an overall surface area of 101.6 cm^2 (1.016dm^2). The anode and the cathode electrodes of the anodizing cell are made of these specimens Chemical solutions were used as follow:

1. Sulfuric acid solution of 98% purity was used as an electrolyte in different concentrations for the anodizing step.
2. For alkaline etching, 5 % NaOH solution was used.
3. For acidic etching, 15 % HNO_3 solution was used.

Different measuring devices were used through the experimental investigation of this study, these devices are as follows: -

(a) An (Avo) meter (type universal Avo meter) was used for adjusting current density that adopted through the experiment. This meter that reads 12 Amp, 1200 V and 100000 Ohm has the capability for implementing in AC and DC systems.

(b) To maintain the temperature of the electrolysis solution at a specified temperature and perform good degree of mixing in the solution, temperature

regulator incorporated with a stirrer (type-zeal) was fixed in the anodizing cell beside the mechanical stirrer of type Heidolph 50110.

(c) To measure the thickness of the anodized film a thickness – testing meter (type posit pilot®) was used.

A rectangular box made of polyethylene to resist the action of sulfuric acid was prepared to roll as an anodizing cell. Aluminum wire jigs designed to hold the anodes and the cathodes were fixed in the cell by racks. Direct and Alternative voltage power supply (type, mi–dual power supply, TF-2158) was incorporated with the anodizing cell to supply current to the electrodes of maximum of 3 Amp and voltage of 30 volt. To maintain good mixing of the electrolyte solution and to prevent temperature layering in the anodizing cell, a mechanical stirrer (type, Heidolph 50110) was employed. Cooling system was installed which consist of a rectangular cooling bath, grant instrument (type SU6) for pumping water and an immersed glass coil. Figure (1) shows a schematic diagram for the anodizing apparatus assembly. To heat up the chemicals at the desired temperature through etching and sealing steps a mantel heater was used. Besides, specimen dryer (type MS) was employed for preparing the anodized specimens after oxidation, to measure thickness.

EXPERIMENTED PROCEDURE INCLUDES

1. Mechanical & chemical pre-treatment step:

Raw material of pure Aluminum and Al-Mg alloy were received in the form of sheets. Each sheet had been cut into small specimens of dimension (100*45*4) mm. Sharp edges of the specimens were chamfered via grinding wheel. For modifying the surface of the specimens, pre anodizing process, the following steps were adopted:

(i) Alkaline Etching: the specimens were etched by dipping the specimens in 5% NaOH solution (density = 1.06 gm/cm^3) for 5 min. at temperature of 45 C^0. Then, the specimens was rinsed by tap water & then by distilled water to ensure the removal of NaOH.

(ii) Acid Etching: after alkaline etching, the specimens were immersed in 15 % HNO_3 solution. (density = 1.085 gm/cm^3) for 10 sec. at room temperature in order to remove the black layer that formed on the surface & also to activate the surface for anodizing step . After that specimens were rinsed with excess water & later by distilled water. Eventually, perfect dryness of the specimens from any existence of moisture was accomplished prior anodizing step.

2. Anodizing step

The anode &the cathode electrodes were well connected to the aluminum wire jigs as they hold tightly by the racks. After, the operating conditions were adjusted predetermined conditions that already designed according to (Central Composite Rotatable Design of Box Wilson). Accordingly the mechanical stirrer, water bath temp, concentration of electrolyte & eventually the current were all justified.

3. Post treatment steep

After completion of the anodizing process, the specimen was lifted from the cell & rinsed with tap water to remove the residual of electrolyte solution from the surface of the specimens. After that ,the specimens was dipped in a flask filled with

distilled water & kept for 20 min .at 95 C^{o} in over to minimize (seal) the initial porosity.

4. Measuring Anodizing Film Thickness:

The technique used for measuring the thickness of the film after each experiment was the eddy current method that was commenced by employing the thickness – testing meter of posi-pilot type. Figure (2) shows samples of experiments.

RESULTS AND DISCUSSION

The last column in Table (5) and (6) show the experimental and predicted thickness of the anodic film. A second order polynomial correlates the four variables (i.e current density, electrolyte concentration, electrolyte temperature and time of exposure) with the thickness of the anodic film.

To postulate the best formal of the proposed model, the coded variables Table (5), (6) will be first fitted through non liner regression analysis to estimate the coefficients of the proposed model. By using the coded data of the central composite rotatable design, Tables (5) and (6) the coefficients of the 2nd order polynomial were estimated by implementing nonlinear regression estimation technique via the statistical software. The number of iterations was terminated when the proportion of variance accounted for was equal to 0.97305 and the correlation coefficient (R) was equal to 0.9864. Tables (7) and (8) had listed these values of the coefficients of the proposed model for pure Aluminum (1000) and Aluminum-Magnesium alloy (5052) as shown below.

Best values were determined using hook and jeeves pattern move technique. The final form of the proposed model for pure Aluminum (1000) and Aluminum – Magnesium alloy (5056) was found as follow respectively:

$$Y = 4.1 + 1.07X_1 - 1.1X_2 + 1.06X_3 + 0.53X_4 - 0.73X_1^2 + 0.19X^2_2 + 0.32X^2_3 + 0.16X^2_4 - 1.2X_1X_2 - 0.15\ X_1X_3 + 2.3X_1X_4 - 1.6X_2X_3 - 3.6X_2X_4 + 0.46X_3X_4. \quad \textbf{…(7)}$$

$$Y = 9.2 + 2.6X_1 - 1.15X_2 - 1.09X_3 + 4.1X_4 - 0.3X_1^2 - 0.8X^2_2 - 0.08X^2_3 - 0.06X^2_4 + 0.2X_1X_2 + 1.1\ X_1X_3 + 2X_1X_4 + 2.8X_2X_3 - 0.13X_2X_4 + 0.3X_3X_4. \quad \textbf{…(8)}$$

EFFECT OF CONCERN VARIABLES

Equation (7) and (8) show thickness dependence of the oxide film on current density (X_1) , electrolyte concentration (X_2) , temperature of the electrolyte (X_3) and time of exposure (X_4) in following sequence : ($X_3>X_1>X_4>X_2$), for pure Aluminum and ($X_4>X_1>X_3>X_2$) for Aluminum-Magnesium alloy. Where: Y is the Objective function (film thickness).

ESTIMATING THE BEST CONDITIONS

It was found from hook and Jeeves method that best values of the studied variables in coded and real form are as listed in Table (9). Figures (3) and (7) show the effect of current density on the film thickness at optimum conditions for concentration, temperature and times of exposure. Rates of film growth over a range of current densities are shown in Figures where the thicker coatings are

formed at higher current densities as expected. As pointed out earlier current densities above 2.5 Amp/dm^2 results in streaking and pitting of the oxide coating. For the successful operation of the bath it is very important that the current be initially raised slowly and steadily. Otherwise, burning of the coating occurs because of the rapid dissolution of the coating in the electrolyte. Increasing the current density 3Amp./dm^2 which was contributed to the great tendency of film built up in higher current density where Increasing the anodizing current at a given temperature increases the coating thickness, the barrier layer thickness and the diameter of the pores decrease which lead to bright color while the coating porosity decreases[17, 24] In general The porosity of anodic film thickness was decreased according to film thickness where the higher film thickness gives low porosity with small diameter of the pores which is darkness in color vice versa.

Figures (4) and (8) illustrate the effect of concentration on the film thickness at optimum conditions for current density, temperature and anodizing times. The amount of aluminum oxide is inversely proportional to the concentration because the increasing in sulfuric acid concentration at a given anodizing voltagelead to increases the current density due to higher solubility of the oxide film. This higher film dissolution is also responsible for the increase of the pore diameter and the coating porosity [24]. Normally, the thickness of the oxide film decreases to a minimum value at which it is concentration at this value prevent the reaction of the oxygen with aluminum, i.e. to produce aluminum oxide. Concentration of the dye bath is determined by the solubility of the dye stuff and also by the intensity of the color required. To reduce the drag out losses the dye baths are operated at 5 to 10 g/l. More dilute solutions are used for very light tones while concentrations in the higher range (8-10 g/l) are used when darker shades are required [18,25]. Also, the statistical analysis of the response function showed that concentration of the electrolyte (X_2) has the smallest effect to prohibit. the film growth in comparison to the other variables that had positive dependencies, i.e. anodizing time (X_4), current density (X_1) and temperature (X_3) since the concentration had a negative dependence, i.e. the value of the coefficient in Equation.(7) and (8) was equal to (1.1) and (- 1.15). The effect of temperature on film thickness at optimum conditions for current density, concentration and anodizing time was monitored in Figures (5) and (9). It was obviously observed that the Increasing in the film thickness is linearly proportional to the anodizing temperature, because of using alternative current density which lead to drop in the corrosion rate during anodizing time where Increasing the temperature at a given anodizing voltage increases both the current density and the coating porosity due to thermal enhanced field assisted dissolution. Additionally, the dissolution of the outer oxide surface is enhanced [19, 24]. The depth of color depends on the rate of diffusion of the dye into the pore channels and getting adsorption on the inside of pore wall. This diffusion is slow process and depends on the nature of the dye stuff, the temperature of the dye bath, the time of treatment in the dye bath. Increase in temperature of the dye bath increase the rate of diffusion into the pores and hence reduce the time of dyeing. However, very high temperature is often used in practice because of the stability of the bath though the dye stuff will be affected [20, 25]. Anodizing time (X_4) had a pronounced effect on film thickness in comparison to other variables. It was obviously observed that the increase in film thickness is linearly proportional to the exposure time within the time of treatment of 60 minutes. The thickness of the

anodic oxide film was plotted as a function of anodizing time Figures (6) and (10) it was obvious that the oxide thickness increased linearly with the time during anodizing process under best conditions [21, 24]. The time of immersion in the dye bath influences the light-fastness of dyed anodic coating. Too short a time inhibits the penetration of dyes into the pore channels and gives only a superficial adsorption on the top layer while too long a time dose not materially affect for production runs. Generally, a time of 5 to 15 minutes with a good degree of agitation of a work or the bath result in uniform dyeing without patchy color provided the dye bath is maintained free of contamination from heavy metal cat ions, oil, grease or hard water[25].

INFLUENCE OF ALLOY COMPOSITION

Alloy composition significantly affects the formation of oxide coating because of the difference in behavior of alloys in the electrolyte. The pores can be seen clearly in sulfuric acid (H_2SO_4) in addition to the cellular structure can be nearly identified as shown in Figures (9) and (10), respectively. The porous oxide layers surface microstructures appear differently where the pores are defined and the distribution is regular. The surface images show pores of varying diameters, some pores seem to have coalesced; therefore it is difficult, from the images, to calculate the exact width of the pores.Based on the comparison of the computerized metallurgical optical microscope technique (CMOMT) for porous anodic alumina (PAA) top view images of aluminum alloy (1000) samples anodized at the maximum conditions of film thickness as shown in Figures (11) and (12). The pulsed current density, electrolyte concentration, reaction temperature and time are four main deciding elements for the structure of porous anodic alumina (PAA) [20, 26]. The positively charged surface layers of anodic coating on aluminum attract the chromophoric anion of the sulphonated dyes. The bond formation with the oxide may be through hydrogen bonding Chelating or ion-exchange. Porosity, viz. the pore diameter, pore depth and pore intensity influences the quality of dyeing. The concentration of sulphric acid electrolyte, which is the most used bath for anodizing, influences the color rating and also unit sealing value [20, 25].

CONCLUSIONS

1. The alloy type effects on the rate of electrolytic coloring deposition process.
2. The anodizing current passed seems to influence the amount of color deposited and the effect is less for alloys than for pure aluminum, indicating that, in the later case, the anodizing current affects in a greater extent the porosity of the film.
3. The current efficiency for coloring deposition during electrolytic coloring at standard conditions is much higher for pure aluminum than for alloys.
4. The oxide film has a lighter color at lower current density where lower values of current density means lighter and fastness color, the darkest color for normal oxide film occurs at higher current density.
5. Anodizing in sulfuric acid electrolyte produces oxide coating which can range from light gold to browns to blacks and also to green.

6. It has found that an aqueous solution of sulfuric acid can be advantageously utilized as an electrolyte for the integral color anodizing of aluminum and its alloys.
7. By visually inspection it was found that the low frequency samples showed a lighter performance of the color than the rest of the electrolytically colored samples.
8. The porosity of anodic film thickness was decreased according to film thickness where the higher film thickness gives low porosity with small diameter of the pores which is darkness in color vice versa.
9. The coating produced is similar to the conventional sulphuric acid coating excepting that the coating is a little brighter and brittle.

REFERENCES

[1]. Adrews,D.G. Trans. Inst. Met. Finish. 58 (1980) 13.
[2]. Barnes,C. Rev. Prog. Color.14 (1989) 127.
[3]. Jelinek,T.W. Galvanotechnik 79 (1988) 60.
[4]. Thorne, N. G. Thompson, R. Furneaux, G.Wood, in: R.S. Alwitt, G.E. Thompson (Eds.), Proc. Symp. on Aluminum Surf. Treatment Technol., TheElectrochem. Society, Pennigton, NJ, 1986, p. 274.
[5]. Doughty, A.S. G.E. Thompson, J.A. Richardson, G.C. Wood, Trans. Inst. Met. Finish. 53 (1975) 33.
[6].Sheasby, P. G.; Pinner, R. The Surface Treatment and Finishing of Aluminum and its Alloys.2 (sixth ed.). Materials Park, Ohio &Stevenage, UK: ASM International & Finishing Publications. ISBN 0-904477-23-1. (2001).
[7]. Adrews,D.G. Bull. Inst. Met. Finish. 58 (1980) 13.
[8]. Barnes,C. Rev. Prog. Color.Relat.Top.14 (1989) 127.
[9].Jelinek, Galvanotechnik 79 (1988) 60.
[10]. Wernick,S. R. Pinner, P.G. Sheasby, The Surface Treatment and Finishing of Aluminum and its Alloys, vols.I, II, ASM International Finishing Publications Ltd, England, 1987.
[11]. Habazaki, H. et al., Corros. Sci. 39 (1997) 731.
[12]. Habazaki, H. K. Shimitzu, P. Skeldon, G.E. Thompson, G.C. Wood, Trans. IMF 75 (1) (1997) 18.
[13]. Baker, B.R. Proc. Symp. on Aluminum Surf. Treatment Technol., TheElectrochem. Society, Pennigton, NJ, 1986, p. 78.
[14]. Gohausen, H.J. G.C. Schoener, Plating Surf. Finish. 2 (1984) 56.
[15]. Sato,T. Plating Surf. Finish. 3 (1991) 70.
[16].Serebrennikova, P. Vanyzek, V.I. Bizss, Electrochim. Acta 42 (1997) 145.
[17].Nahidh W. Kaseer, Ali Hussin A., Talib M. Naieff, Anodizing of Aluminum-Magnesium Alloy 5052, Iraqi Journal of Chemical and Petroleum Engineering , vol. 3 (2002) 35-44.
[18].Nahidh W. Kaseer, Ali Hussin A., Talib M. Naieff, The determination of the variables of high response on the anodizing of aluminum-Magnesium alloy 5052 (statistical analysis), Iraqi Journal of Chemical and Petroleum Engineering , vol. 3 (2002) 25-30.

[19].Talib M. Naieff, Sami A. Ajeel, Nissreen Sabah, Using alternative current (A.C) for anodizing process, Eng. and Tech. Journal, 2005, vol. 24, no.3 (307-327).
[20].Talib M. Naieff, Khalid H. Rashid, Comparative Study for Anodizing Aluminum Alloy 1060 by Different Types of Electrolytes Solutions, first scientific conference on modern technologies in oil and gas refinery - Chemical Eng.Dept., University of technology and midland refineries company .
[21].Box and George E.P., "statistics experimenters", New York (1978).
[22].Trethewy K.R. &J .chamberlain "corrosion for science & engineering" long man group limited (1996).
[23].Scott B. A., Ph. D. Thesis, University of London (1945).
[24].Tsangaraki-Kaplanoglou, S. Theohari, Th. Dimogerontakis, N. Kallithrakas-Kontos, Y. Wang, H. Kuo, S. Kia, Surf. Coat. Technol. 200 (2006) 2634 – 2641.
[25].C Rajagopal, KI Vasu." Conversion Coating a Reference for Phosphating, Chromoting and Anodizing Processes"© Copyright (2000), Tata McGraw-Hill Publishing Company Limited.
[26].Zhao, N. and Jiang, X.,"Effects of Anodizing Conditions on Anodic Alumina Structure", J. Mater. Sci., Springer Science, China, No.2, (2007), p.3878–3882.

Table (1): working range of coded and corresponding real variables

Coded level	Current density (Amp./dm^2)	Concentration (equiv/Lit.)	Temperature (C^o)	Duration time (min)
-2	2	2	15	20
-1	2.25	3	17.5	30
0	2.5	4	20	40
1	2.75	5	22.5	50
2	3	6	25	60

Table (2): Sequence of experiments according to central composite design.

EXP. NO.	Coded variable				Real variable			
	X_1	X_2	X_3	X_4	Current Density (Amp./dm^2)	Concentration (equiv/liter)	Temperature (C^o)	Time (min)
1	- 1	-1	-1	-1	2.25	3	17.5	30
2	1	-1	-1	-1	2.75	3	17.5	30
3	- 1	1	-1	-1	2.25	5	17.5	30
4	1	1	-1	-1	2.75	5	17.5	30
5	- 1	-1	1	-1	2.25	3	22.5	30

6	1	-1	1	-1	2.75	3	22.5	30
7	- 1	1	1	-1	2.25	5	22.5	30
8	1	1	1	-1	2.75	5	22.5	30
9	-1	-1	-1	1	2.25	3	17.5	50
10	1	-1	-1	1	2.75	3	17.5	50
11	- 1	1	-1	1	2.25	5	17.5	50
12	1	1	-1	1	2.75	5	17.5	50
13	- 1	-1	1	1	2.25	3	22.5	50
14	1	-1	1	1	2.75	3	22.5	50
15	- 1	1	1	1	2.25	5	22.5	50
16	1	1	1	1	2.75	5	22.5	50
17	- 2	0	0	0	2	4	20	40
18	2	0	0	0	3	4	20	40
19	0	-2	0	0	2.5	2	20	40
20	0	2	0	0	2.5	6	20	40
21	0	0	-2	0	2.5	4	15	40
22	0	0	2	0	2.5	4	25	40
23	0	0	0	0	2.5	4	20	20
24	0	0	0	-2	2.5	4	20	60
25	0	0	0	2	2.5	4	20	40
26	0	0	0	0	2.5	4	20	40
27	0	0	0	0	2.5	4	20	40
28	0	0	0	0	2.5	4	20	40
29	0	0	0	0	2.5	4	20	40
30	0	0	0	0	2.5	4	20	40
31	0	0	0	0	2.5	4	20	40

Table (3) listed chemical Composition of aluminum magnesium alloy 5056.

Specification		Approximate percent composition					
UK	USA	Cu	Mg	Si	Mn	Cr	Other
N4	5052	-	2.5	0.4_{max}	-	0.25	-

Table (4) chemical composition of aluminum magnesium Alloy (5056) [22].

Cu %	Fe %	Mn %	Zn %	Mg %	Si %	Al %

0.006	0.222	0.037	0.010	2.3711	0.100	97.25

Table (5): Sequence of experiments for pure Aluminum (1000) according to central composite design.

Exp. No.	Coded variable				Real variable				Exp. Thick.	Predicted Thick.
	X_1	X_2	X_3	X_4	Current density (Amp./dm^2)	Conc. (eq. /Lit.)	Temp. (C^o)	Time (min)	Y(Micron)	Y (Micron)
1	-1	-1	-1	-1	2.25	3	17.5	30	3.1	1.6
2	1	-1	-1	-1	2.75	3	17.5	30	1.2	1.7
3	-1	1	-1	-1	2.25	5	17.5	30	11.5	12.3
4	1	1	-1	-1	2.75	5	17.5	30	7	7.6
5	-1	-1	1	-1	2.25	3	22.5	30	6.5	6.3
6	1	-1	1	-1	2.75	3	22.5	30	5.6	5.8
7	-1	1	1	-1	2.25	5	22.5	30	9.9	10.6
8	1	1	1	-1	2.75	5	22.5	30	6.3	5.3
9	-1	-1	-1	1	2.25	3	17.5	50	3.1	4.3
10	1	-1	-1	1	2.75	3	17.5	50	15.3	13.8
11	-1	1	-1	1	2.25	5	17.5	50	1.5	0.54
12	1	1	-1	1	2.75	5	17.5	50	4.7	5.1
13	-1	-1	1	1	2.25	3	22.5	50	12.2	10.9
14	1	-1	1	1	2.75	3	22.5	50	20.4	19.8
15	-1	1	1	1	2.25	5	22.5	50	1	0.7
16	1	1	1	1	2.75	5	22.5	50	3.9	4.7
17	-2	0	0	0	2	4	20	40	4.5	4.9
18	2	0	0	0	3	4	20	40	9.2	9.1
19	0	-2	0	0	2.5	2	20	40	5.9	7
20	0	2	0	0	2.5	6	20	40	3.5	2.6
21	0	0	-2	0	2.5	4	15	40	3.4	3.2
22	0	0	2	0	2.5	4	25	40	7	7.5
23	0	0	0	0	2.5	4	20	20	10	9.5
24	0	0	0	-2	2.5	4	20	60	10.9	11.7
25	0	0	0	2	2.5	4	20	40	4.1	4.1
26	0	0	0	0	2.5	4	20	40	4.1	4.1
27	0	0	0	0	2.5	4	20	40	4.1	4.1
28	0	0	0	0	2.5	4	20	40	4.1	4.1
29	0	0	0	0	2.5	4	20	40	4.1	4.1
30	0	0	0	0	2.5	4	20	40	4.1	4.1
31	0	0	0	0	2.5	4	20	40	4.1	4.1

Table (6): Sequence of experiments for Aluminum – Magnesium alloy (5056) according to central composite design.

Exp. No.	Coded variable				Real variable				Exp. Thick.	Predicted Thick.
	X_1	X_2	X_3	X_4	Current density (Amp./dm^2)	Conc. (eq./Lit.)	Temp. (C^o)	Time (min)	Y (Micron)	Y (Micron)
1	-1	-1	-1	-1	2.25	3	17.5	30	8.3	8.2
2	1	-1	-1	-1	2.75	3	17.5	30	6.9	6.7
3	-1	1	-1	-1	2.25	5	17.5	30	3.5	4.1
4	1	1	-1	-1	2.75	5	17.5	30	3.3	3.4
5	-1	-1	1	-1	2.25	3	22.5	30	1.4	1.4
6	1	-1	1	-1	2.75	3	22.5	30	4.2	4.4
7	-1	1	1	-1	2.25	5	22.5	30	1.5	0.67
8	1	1	1	-1	2.75	5	22.5	30	4.3	4.5
9	-1	-1	-1	1	2.25	3	17.5	50	12.2	12.2
10	1	-1	-1	1	2.75	3	17.5	50	17.6	18.7
11	-1	1	-1	1	2.25	5	17.5	50	7.5	7.5
12	1	1	-1	1	2.75	5	17.5	50	14.6	14.9
13	-1	-1	1	1	2.25	3	22.5	50	6.5	6.7
14	1	-1	1	1	2.75	3	22.5	50	18.2	17.8
15	-1	1	1	1	2.25	5	22.5	50	5	5.4
16	1	1	1	1	2.75	5	22.5	50	17	17.3
17	-2	0	0	0	2	4	20	40	3.1	3.1
18	2	0	0	0	3	4	20	40	14.3	13.3
19	0	-2	0	0	2.5	2	20	40	8.8	8.5
20	0	2	0	0	2.5	6	20	40	4.3	3.9
21	0	0	-2	0	2.5	4	15	40	12.4	11.6
22	0	0	2	0	2.5	4	25	40	7.1	7.2
23	0	0	0	0	2.5	4	20	20	1	1.1
24	0	0	0	-2	2.5	4	20	60	18.7	17.9
25	0	0	0	2	2.5	4	20	40	9.8	9.8
26	0	0	0	0	2.5	4	20	40	9.8	9.8
27	0	0	0	0	2.5	4	20	40	9.8	9.8
28	0	0	0	0	2.5	4	20	40	9.8	9.8
29	0	0	0	0	2.5	4	20	40	9.8	9.8
30	0	0	0	0	2.5	4	20	40	9.8	9.8
31	0	0	0	0	2.5	4	20	40	9.8	9.8

Table (7): Coefficient of the proposed model for pure Aluminum (1000)

Coeff.	B_0	B_1	B_2	B_3	B_4	B_{11}	B_{22}	B_{33}	B_{44}	B_{12}	B_{13}	B_{14}	B_{23}	B_{24}	B_{34}
Value	4.1	1.07	-1.1	1.06	0.53	0.73	0.19	0.32	1.6	-1.2	-0.15	2.3	-1.6	-3.6	0.46

Table (8): Coefficients of the proposed model for (Aluminum – Magnesium alloy 5056).

Coeff.	B_0	B_1	B_2	B_3	B_4	B_{11}	B_{22}	B_{33}	B_{44}	B_{12}	B_{13}	B_{14}	B_{23}	B_{24}	B_{34}
Value	9.8	2.6	-1. 15	-1.09	4.1	-0.3	-0.8	-0.08	-0.06	0.2	1.1	2	2.8	-0.13	0.3

Table (9): Coded and Real Optimum Value of Variables.

Variables	Optimum coded values for pure Aluminum	Optimum real value for pure Aluminum	Optimum coded value for Al-Mg alloy	Optimum real value for Al-Mg alloy
Current Density (Amp/dm^2)	$X_1=2$	$X_1=3$ Amp/dm^2	$X_1=2$	$X_1=3$ Amp/dm^2
Concentration (equi./Lt)	$X_2=-2$	$X_2=2$ Normality	$X_2=-2$	$X_2=2$ Normality
Electrolyte Temperature (C^0)	$X_3=2$	$X_3=25$ Centigrade	$X_3=2$	$X_3=25$ Centigrade
Time of Exposure (min)	$X_4=2$	$X_4=60$ minute	$X_4=2$	$X_4=60$ minute

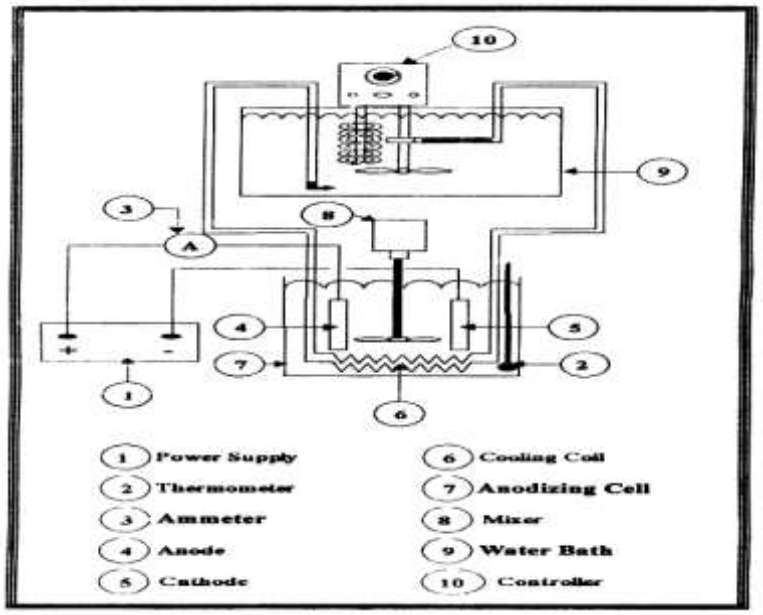

Figure (1): Anodizing experimental units.

Figure (2) sample of experiments.

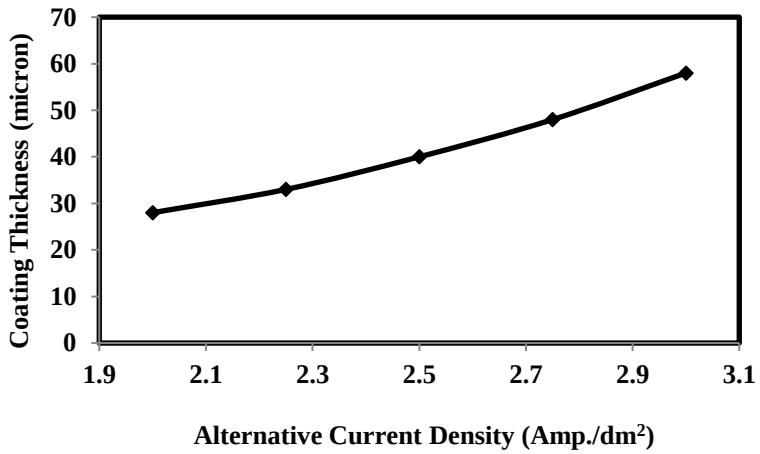

Figure (3): Effect of Alternative Current density on coating thickness at optimum conditions for pure Aluminum.

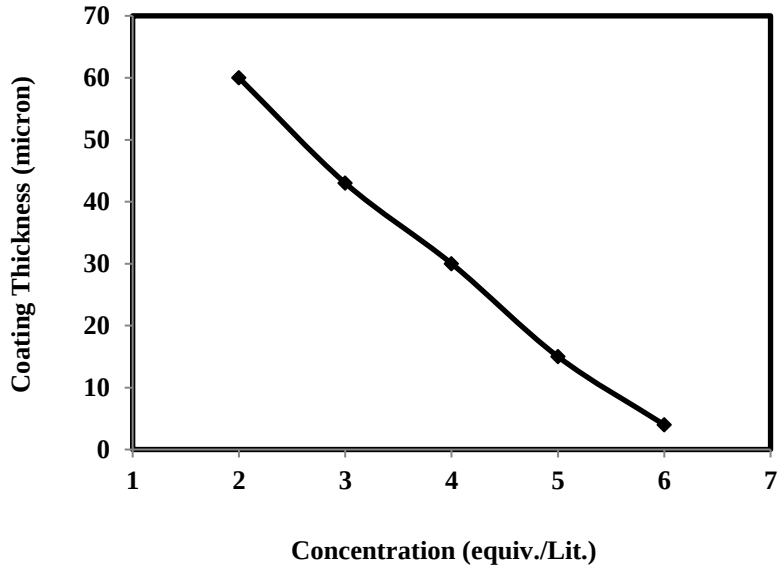

Figure (4): Effect of concentration on coating thickness at optimum conditions for pure Aluminum.

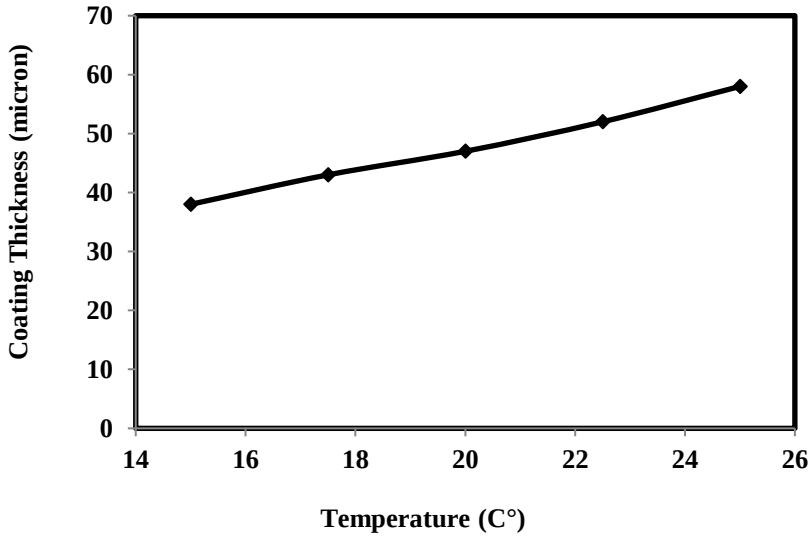

Figure (5): Effect of temperature on coating thickness at optimum conditions for pure Aluminum.

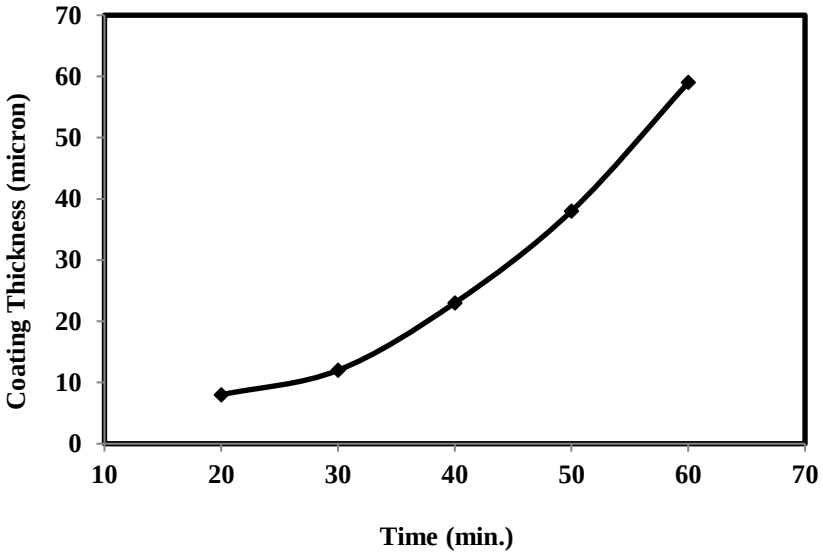

Figure (6): Effect of time on coating thickness at optimum conditions for pure Aluminum.

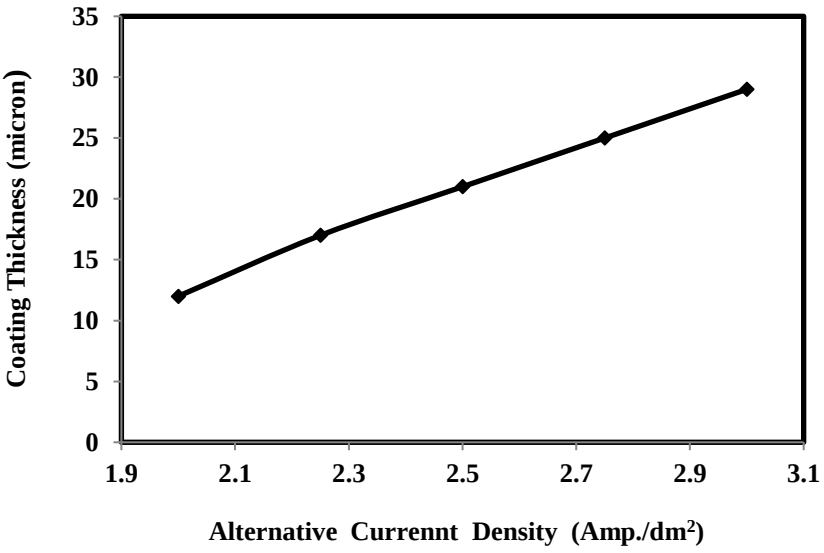

Figure (7): Effect of Alternative Current density on coating thickness at optimum conditions for (Al-Mg) alloy 5056.

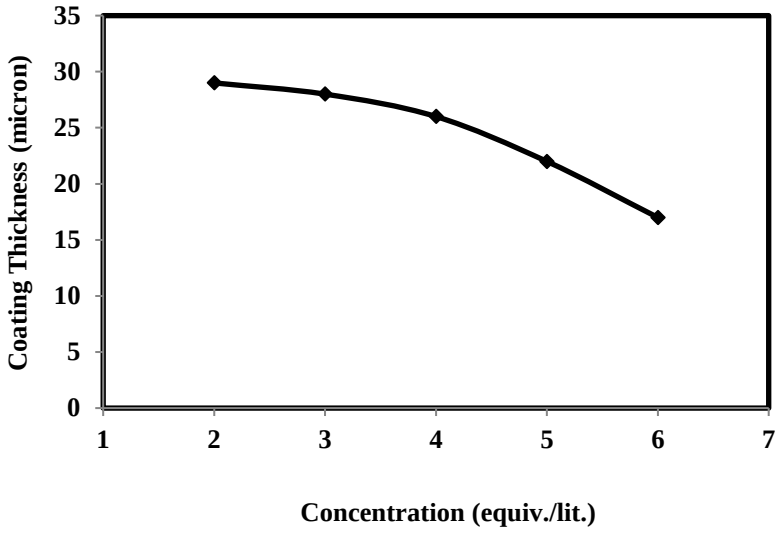

Figure (8): Effect of concentration on coating thickness at optimum conditions for (Al-Mg) alloy 5056.

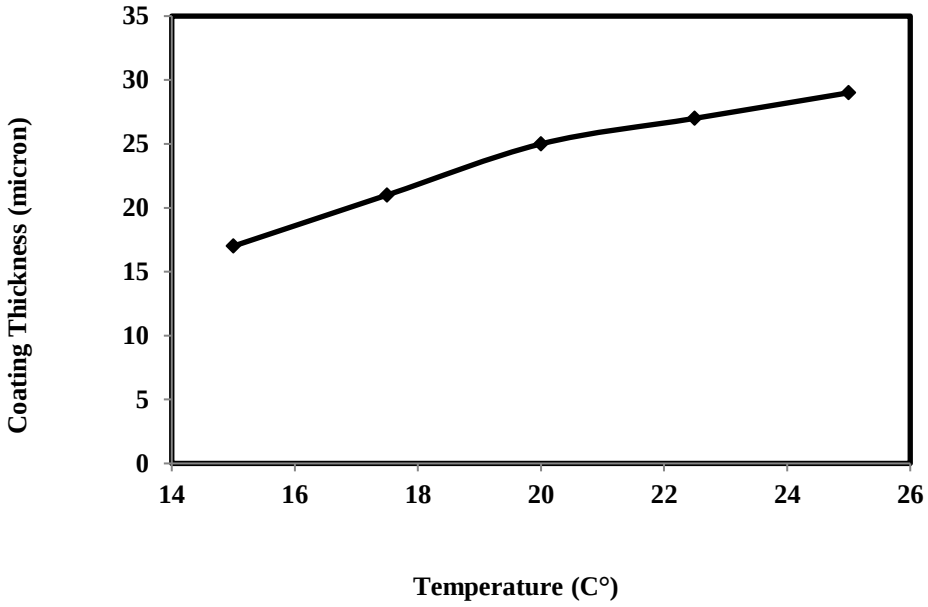

Figure (9): Effect of temperature on coating thickness at optimum

conditions for (Al-Mg) alloy 5056.

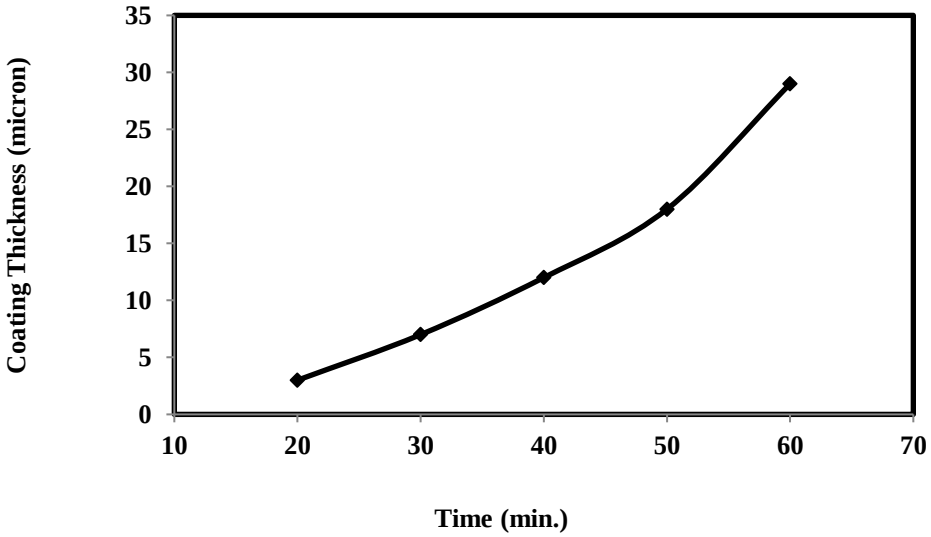

Figure (10): Effect of time on coating thickness at optimum conditions for (Al-Mg) alloy 5056.

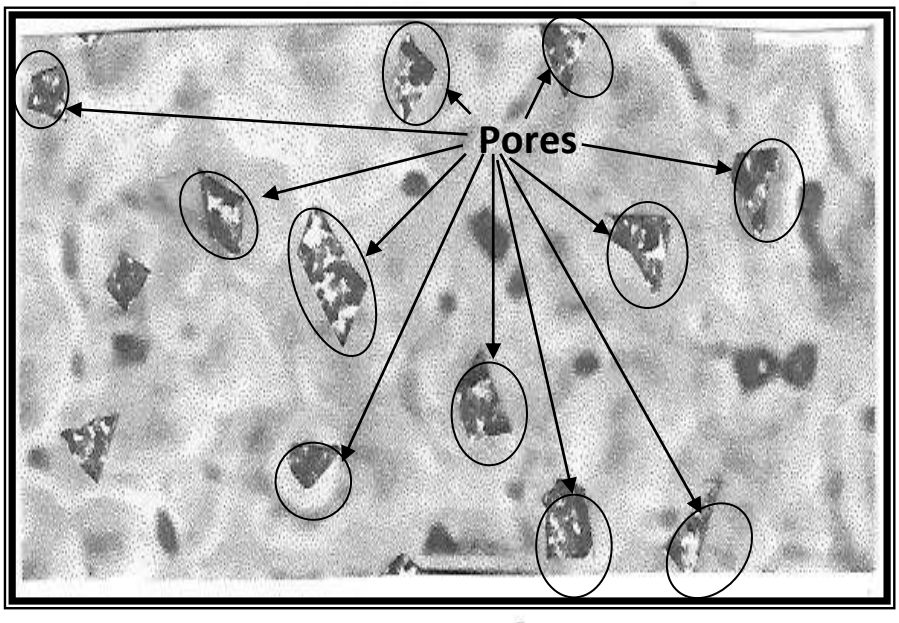

Figure (11): Surface microstructure of porous anodic alumina at the optimum conditions for pure Aluminum.

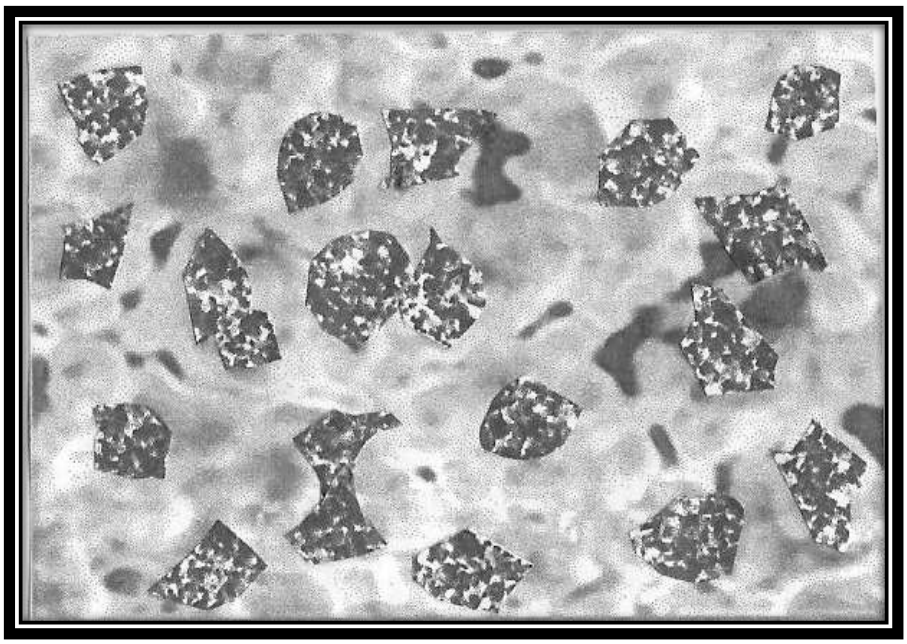

Figure (12): Surface microstructure of porous anodic alumina at the optimum conditions for (Al-Mg) alloy 5056.