

Comparative Study for Anodizing Aluminum Alloy 1060 by Different Types of Electrolytes Solutions

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ABSTRACT

The characteristics of the anodic film for aluminum alloy (1060) have been investigated by using different types of electrolytes solutions oxalic acid ($C_2H_2O_4 \cdot 2H_2O$), phosphoric acid (H_3PO_4), boric acid (H_3BO_3) and tartaric acid ($C_4H_6O_6$).

The effects of three variables were examined to check response of anodic film thickness; The range of these variables as follows: acid concentration ranging between 10 – 20 wt %, voltage ranging between 11–15 V and time of anodizing 20–60 min.. The electrochemical cell was kept at 27 °C.

The experimental results show that the anodizing film thickness was affected by concentration of different electrolytic acidic solutions, anodizing voltage and time of anodizing according to the effects of each electrolyte.

It might be concluded that the film thickness of the anodic film increased with increasing time and voltage of anodizing and decreased with increasing acid concentration. In general, it was found that the anodic film thickness increases to maximum limit at 60 min. in oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) 10 wt %, phosphoric acid (H_3PO_4) 10 wt % and tartaric acid ($C_4H_6O_6$) 10 wt %, respectively. As for boric acid (H_3BO_3) 10 wt % with 0.3 % borax the film thickness increasing up to maximum limit at 50 min. and after this time the decreasing in film thickness gradually was happened.

Computerized metallurgical optical microscope technique (CMOMT) was employed at the maximum film thickness conditions for each sample to observe surface microstructure for the formed anodic film.

It was shown that the type of electrolyte affects on the characteristics and surface microstructure of the anodic oxide layer for aluminum alloy (1060).

The study shows that the porosity of anodic film thickness was decreased according to film thickness where the higher film thickness gives low porosity vice versa with respect to oxalic

acid ($C_2H_2O_4 \cdot 2H_2O$) and phosphoric acid (H_3PO_4). As for boric acid (H_3BO_3) and tartaric acid ($C_4H_6O_6$) just the barrier layer was built.

Keywords: Aluminum Alloy (1060), Anodizing, Different Types of Electrolytes, Oxalic Acid, Phosphoric Acid, Boric Acid, Tartaric Acid, Borax, Anodic Oxide.

Nomenclature

A	Ampere
AAFs	Anodic alumina films
CMOMT	Computerized metallurgical optical microscope technique
M	mega
Pa	pascal
PAA	porous anodic alumina
pH	Acidic function
V	Volt
Å	angstrom
μ	micron

Introduction

Aluminum alloy (1060), 99.60 % aluminum or more, used in chemical and electrical fields. Excellent corrosion resistance, workability, thermal and electrical conductivity and low mechanical properties ⁽¹⁾.

Aluminum alloy (1060) has a room-temperature minimum tensile strength of 75 MPa and yield strength of 25 MPa. Iron and silicon are the major impurities. Commercial purity metal (99.00 to 99.80%) is available in three purities and a range of work-hardened grades, for a wide variety of general applications plus a special composition for electrical purposes. High-purity aluminum is used for many electrical and process equipment applications ⁽²⁾.

Anodizing can be performed in borate or tartrate baths in which aluminum oxide is insoluble. In these processes, the coating growth stops when the part is fully covered, and the thickness is linearly related to the voltage applied. These coatings are free of pores, relative to

the oxalic and phosphoric acid processes. The anodizing of aluminum that leads to a porous structure is usually performed in electrolytes containing sulfuric, oxalic or phosphoric acid ⁽³⁾. This type of coating is widely used to make electrolytic capacitors, because the thin aluminum films (typically less than 0.5 μm) would risk being pierced by acidic processes ⁽⁴⁾.

Bath electrolytes are selected in which the oxide is insoluble, or dissolves at a slower rate than it deposits, and then an adherent oxide layer grows. The bath composition is the primary determinant of whether the film will be barrier or porous. Barrier oxide grows in near neutral solutions in which aluminum oxide are hardly soluble, most commonly ammonium borate, phosphate, or tartrate compositions. Porous oxide grows in acid electrolytes in which oxide can not only be deposited but also dissolves ⁽⁵⁾.

The anodic film produced in phosphoric acid have larger pore diameter than in conventional sulfuric acid films. This greater diameter provides a better conducting path and it is for this reason that phosphoric acid film has been used as one of the methods for pretreating aluminum prior to electroplating due to presence of non-hydrolyzable phosphates thus allows the extremely strong adhesion of organic products. Compared with the sulfuric acid film, the practicable total thickness (up to 6 μm) is less. This is due to the greater solubility of aluminum oxide in phosphoric acid anodizing solution compared with sulfuric acid ^(6,7).

Recently, attention has been paid on the effects of the electrolytic solution composition on the properties of the layers produced by anodic oxidation. It is known that some compounds such as phosphate, fluoride, tartrate and borate can form stable products, such as Al PO_4 or Al F_3 or $\text{Al (C}_4\text{H}_5\text{O}_6)_3$ and Al BO_3 , respectively, that act as barrier layers and protect aluminum alloy substrate ⁽⁸⁾.

Forno and Bestetti ⁽⁹⁾ were investigated the influence of electrolytic solution composition on the structure and corrosion properties of the anodic oxide. The optimal electrolyte solution suitable to produce the best corrosion resistant oxides consists of KOH 3 M, Na_3PO_4 0.21–0.25 M and $\text{Al (NO}_3)_3$ 0.15 M.

Thompson ⁽¹⁰⁾ indicates that the film thickness increases as the time increases in the range between 25–60 minute, moreover increasing the time of anodizing to more than 60 minute has no significant effect. In this case, the formation rate of anodic coating is equal to the dissolution rate of the anodic coating.

Sponere ⁽¹¹⁾ found in his study that the maximum film thickness obtained with acid concentration of 10 – 30 % is at 10 % where at 30 % it is the lowest value.

Tope ⁽¹²⁾ shows in his study that the film thickness reaches a maximum value at about 10 – 12 % concentration, this is due to low solvent action while an additional increase in acid concentration causes a reduction in the thickness which reaches a minimum value at 35–65%.

The aim of this work is to achieve comparative study for the characteristics of the anodic film thickness growth of aluminum alloy (1060) by using different types of electrolytic acidic solutions such as oxalic acid ($C_2H_2O_4 \cdot 2H_2O$), phosphoric acid (H_3PO_4), boric acid (H_3BO_3) and tartaric acid ($C_4H_6O_6$).

Experimental Work

High purity (99.60 %) aluminum alloy (1060) sheets ($30 \times 20 \text{ mm}^2$) with 1mm thickness were used as the raw material and stainless steel sheet type 304 with dimensions ($30 \times 20 \times 1 \text{ mm}$) was used as cathode. Anodic alumina films AAFs were prepared by anodic oxidation was carried out in an oxalic acid, a phosphoric acid, a boric acid with 0.3% borax and a tartaric acid with ammonium hydroxide in pH = 5 solutions. Prior to anodizing, the aluminum sheets were chempolished by dipping in a 10 wt% NaOH solution for 5 minutes at temperature of 45°C . Subsequently, the sheets were desmuted in 5 vol. % nitric acid solution for about 5 minutes at 25°C to remove the black layer that formed on the surface and to activate the surface for the anodizing stage. The pretreated Al sheets were anodized to form AAFs under appropriate anodizing voltages (11–15V) in acid concentrations (10–20 wt %) and time of anodizing (20–60 min.) at constant temperature of 27°C . Subsequently, the surface film was chemically removed in the mixture solution of phosphoric acid (0.4 mol/L) and chromic acid (0.2 mol/L). The electrochemical cell is open to air and the electrodes distance of 4 cm.

The surface microstructures of AAFs for samples at the maximum film thickness conditions for each electrolyte were characterized by using a computerized metallurgical optical microscope technique (CMOMT), (Type MeF₂), (CarlInsize Company – (Instruments Analytical, W. Germany, for analysis of the coatings)) with digital camera. The coatings were examined visually under (5X) magnification power. This test was achieved in Minerals and Production Engineering Department in University of Technology.

Analysis of these samples was carried out using (spark technique) in Ministry of Sciences and Technology. Table (1) shows the result of the analysis of shows the aluminum alloy (1060) used in this work. Table (2) presents a summary of the maximum film thickness results in

terms of compositions and concentrations of anodizing electrolytes at different times and constant voltage 13 V while Table (3) presents a summary of the maximum film thickness results in terms of compositions and concentrations of anodizing electrolytes at different voltages and constant time 30 min. Figure (1) shows schematic diagram for the electrochemical system for anodizing work. pH meter calibration (Type Transmitter 6320, Electronic Instruments limited, Chertsey Surrey England) was carried out by using buffer solutions (4,7,9) before working start. This work was achieved in laboratories of Chemical Engineering Department / University of Technology.

Tests for Anodic Film

Electrical Test

A simple electrical circuit was designed to inspect the surface coating of aluminum alloy (1060) and check if there is any damage or crack in the anodic surface. The equipment is as illustrated in Figure (2). The resistor is adjusted so that brush contact and the probe are directly connected current of 1 A passes. With the pointed probe making effective contact on to the aluminum, if there are any crack or disconnect in the surface layer the circuit is closed and the current is passed. This test was achieved in Ministry of Sciences and Technology.

Chemical Test

Chemical test was carried out to make sure that the entire surface was coated without any damage; the solution used for this test consisted of (Copper sulfate 20 g, Hydrochloric acid 20 ml and Water 1 liter). The time for immersion was 5 min. at 15–20°C. The reagent does not affect an anodic film; however black spots appear where no anodic film is present. This method will also detect cracks in the coating caused by overheating or bending. This test was carried out at Ministry of Sciences and Technology.

Coating Thickness Test

The coating thickness was calculated by using (Gravimetric determination of coating weight and thickness) according to the standard test method (ASTM B 680-80) (G.S. Frankel.2004), can be calculated from the weight loss measured in equation (1) ^(6, 13).

$$Y = \frac{(W_2 - W_3) \times 10^4}{A \times \rho} \dots\dots (1)$$

where:

Y = coating thickness in micron.

W_2 = weight of a sample with anodic coating in (g).

W_3 = weight of a sample after stripping in (g).

A = surface area (dm^2).

ρ = density in (g/cm^3) is about 2.4 for unsealed coating ⁽⁶⁾.

Results and Discussion

The effect of anodizing time on film thickness

Figure (3) shows the effect of time on film thickness for two concentrations of oxalic and phosphoric acid solutions 10 and 20 wt %, voltage of anodizing and temperature are constant, it can be seen that initially there is a rapid and exponentially increase in the film thickness of solution 10 wt %. During anodizing there is a continuous, thickness growth of the anodic film and dissolution by chemical attack and the resulted film thickness is proportional to the treatment time when anodizing at constant applied potential it depends upon Faraday's Law, which states that the oxide formed is proportional to the electric charge passed (Amp/sec) through the anode and due to the greater solubility of aluminum oxide and a dissolution by chemical attack in oxalic acid solution at high acid concentration 20 wt% in addition, oxalic acid is oxide-solvent electrolyte and formed porous oxide due to in which oxide can not only be deposited but also dissolves and the increase in concentration limitates the maximum film thickness due to the higher dissolving power of the concentrate solutions ⁽⁵⁾. The rate of thickness growing depends of several factors such as: type of electrolyte, applied voltage, treatment time, as well as the alloy composition and the increase in concentration limitates the maximum film thickness due to the higher dissolving power of the concentrate solutions with presence the relationship between the oxide formation and dissolution rates for the aluminum–alumina–electrolyte system ⁽¹⁴⁾. Therefore, the anodic film produced in phosphoric acid have larger pore diameter in comparison with oxalic acid film due to the effect of oxide-solvent action electrolyte resulted to form greater pore diameter in a porous layer.

Figure (4) shows the effect of time on film thickness for two concentrations of boric and tartaric acid solutions 10 and 20 wt %, voltage of anodizing and temperature are constant, it can be seen that the anodic oxides produced by boric acid 10 wt % at 20, 30, 40 and 50 min. have increased thicknesses, ranging between 0.126 and 0.494 μm . After 50 min., the oxide

thickness was gradually decreased, because the oxide dissolution is predominant compared to growth for longer times at 60 min. becomes 0.438 μm . Therefore, 50 min. of anodizing time is considered the best compromise in terms of time and thickness in addition, it can be seen that the film thickness increased as the time increased until it reaches about 50 min. which is consistent with Faraday's law then decreased as the time increased. At time 50 min. the formation rate of anodic coating is equal to the dissolution rate of the anodic coating. Thus the maximum time is equal to 50 min. ⁽¹⁵⁾. The film thickness formed in tartaric acid electrolyte 10 wt % differs from the film thickness formed in boric acid electrolyte 10 wt %, but the film growth formed in tartaric acid electrolyte 20 wt % there is gradually a slight exponentially increase by a small growing in the rate of thickness growth that as the same behavior in comparison with the film growth in boric acid electrolyte 20 wt %, resulted to finally the thickness remains exponentially increase for longer times at 60 min. in tartaric acid electrolyte 20 wt % in spite of continued application of applied voltage 13V.

From Figure (4), it can be seen that the film thickness for tartaric acid decreases with increasing acid concentration due to a specific role of the species on the barrier layer, which contributes to the enhancement of the performance in term of the anodic film and presence these compounds of the tartaric acid also governs the properties of formed oxide layer ⁽¹⁶⁾.

Figures (3) and (4) show the effect of time on film thickness for different types of electrolytes solutions for two acid concentrations 10 and 20 wt %, voltage of anodizing and temperature are constant, it can be seen that the increase in film thickness is proportional to increase in the time of anodizing. Normally, the film thickness is proportional to time due to oxide growth is predominant compared to dissolution for longer times. Henely ⁽⁶⁾ proved that the relationship between the film thickness and time of anodizing is listed as follows:

$$Thickness(\mu m) = \frac{Current\ density\ (A/dm^2) \times Time\ (min.)}{3} \dots\dots (2)$$

From indicated figures also that the film thickness is a function of time, so the maximum value can be obtained at longer time of anodizing. This behavior can be attributed to: When the time increased, the formation rate of film thickness increased, because the anodic layer formation process on aluminum surface include three essential stages where these need to time, during these stages can show time influence on film thickness, essential stages for anodic layer include ⁽¹⁵⁾:

1. Attacked stage of electrolytic solution to anode surface.

2. Formation stage of barrier layer.
3. Formation stage of hydrate layer (porous layer).

The effect of anodizing potential on film thickness

Figure (5) shows the effect of voltage on film thickness for two concentrations of oxalic and phosphoric acid solutions 10 and 20 wt %, time of anodizing and temperature are constant, it presents that the film thickness decreases with increasing acid concentration and generally increases with voltage increasing. Normally, the film thickness is proportional to voltage due to the reaction of the oxygen ion with aluminum ion, i.e. to produce aluminum oxide ⁽⁴⁾ as indicated by Sulka and Stepniowski ⁽¹⁷⁾ were investigated a steady-state formation of porous anodic alumina at the potentiostatic regime occurs at a constant current density. According to the Faraday's law, the thickness of oxide layer formed during anodizing of aluminum in oxalic acid is directly proportional to current density and anodizing time when Faradaic current efficiency equals 100%. For a given duration of the process (30 min. or 60 min.), the thickness of oxide layer increases with increasing current density and consequently with increasing anodizing potential. Therefore, with increasing anodizing potential, increasing of the oxide layer thickness is observed for all studied concentrations. It presents that the film thickness is almost exponential with the voltage in the given electrolyte. At lower voltage, the concentration of the phosphoric acid effects weakly on the film thickness, whereas it becomes more and more obviously along with the increase of the voltage.

Figure (6) indicates the effects of formation voltage on film thickness for two concentrations of boric and tartaric acid solutions 10 and 20 wt %, time of anodizing and temperature are constant. The formed film thickness of boric acid solution 20 wt % at 11 V was 0.123 μm , while it was 0.231 μm for the film formed at 15 V and of boric acid solution 10 wt % at 11V was 0.134 μm , while it was 0.409 μm for the film formed at 15 V. Generally, it is believed that the film thickness is proportional to the formation voltage. However, the film thickness increased with increasing formation voltage. Therefore, it is clear that the electric field strength decreases with decreasing formation voltage. The formed film thickness of boric acid decreases with increasing acid concentration and generally logarithmic increases

with voltage increasing until it reaches about 14 V only reaction of the oxygen ion with aluminum ion, i.e. to produce aluminum oxide⁽⁴⁾. This is in good agreement with that shown by Ono, Wada and Asoh⁽¹⁸⁾ were investigated the effect of formation voltage on the film thickness of anodic barrier film formed on aluminum by anodizing in 0.5 mol dm⁻³ boric acid-0.05mol dm⁻³ borate solutions. The transport number of Al⁺³ of the film formed at 80 V was 0.44, while it was 0.34 for the film formed at 5 V and the transport number of Al⁺³ decreased with decreasing voltage although the films were formed at the same current density. The thickness of the oxide films produced in a given time depends only on the applied anodizing voltage and therefore can be controlled because the rate of thickness growing depends of several factors such as: type of electrolyte, applied voltage, treatment time, etc. for this type of oxide film is non-porous and is called an anodic barrier-layer. This is in good agreement with that shown by Hass and Scott⁽¹⁹⁾ were investigated the effect of voltage on the thickness of anodic barrier film formed on aluminum by anodizing in 3% ammonium tartrate solutions as a function of voltage for 30 sec, 2 and 15 min. anodizing time. The thickness increases linearly with the applied voltage. Layers produced in 30 sec have a thickness of 12.2 Å / V and in 2 min. have a thickness of 13 Å / V. The thickness increase in the next 15 min. is only 5 %.

From Figures (7) and (8), we show anodic film thickness formed for each sample in different types of electrolytes at the maximum conditions in the order: Oxalic acid (C₂H₂O₄.2H₂O) > Phosphoric acid (H₃PO₄) > Tartaric acid (C₄H₆O₆) > Boric acid (H₃BO₃). The anodization in oxalic acid (Process 1) list in Table (2) produces a coating with thickness of 14 μm. It is obvious that only some electrolytes, such as oxalic and phosphoric acid, contribute to the layers with significant thickness. Other electrolytes, such as boric and tartaric, cannot thicken the anodic coatings significantly.

The surface microstructure characteristics of anodic film

Characteristics of the porous anodic film

The pores can be seen clearly in both anodic oxides images of oxalic acid (C₂H₂O₄.2H₂O) and phosphoric acid (H₃PO₄) 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 and the pores are well 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. On top of the samples there is a layer of porous anodic alumina (PAA) was existed where the void percentage, or porosity, increases linearly with pore diameter in the order:

Anodic film fabricated in (H_3PO_4) electrolyte > Anodic film fabricated in ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) electrolyte.

Based on the comparison of the computerized metallurgical optical microscope technique (CMOMT) for porous anodic alumina (PAA) top view images of aluminum alloy (1060) samples anodized at the maximum conditions of film thickness at constant anodizing voltage 13 V in ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and (H_3PO_4) electrolytes as shown in Figures (9) and (10). The porous oxide layers microstructure appears differently, the higher film thickness (14.571 μm) formed in ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) electrolyte gives low porosity in comparison with the higher film thickness (8.381 μm) formed in (H_3PO_4) electrolyte gives high porosity because these differences could be attributed to an electrolyte chemical action along the cell walls that causes chemical dissolution of the oxide layer, considerably enhances with a prolonged anodizing time. It is generally accepted that for porous anodic alumina (PAA) formed in ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) electrolyte at potentiostatic regime, the pore diameter (D_p) is linearly proportional to the applied anodizing potential (U) as follows ⁽¹⁶⁾:

$$D_p = \lambda_p U \quad \dots\dots (3)$$

With a proportionality constant (λ_p) of about 0.4 nmV^{-1} for anodizing ⁽¹⁴⁾.

The voltage, electrolyte concentration and reaction temperature are three main deciding elements for the structure of porous anodic alumina (PAA). The increase of the three parameters can enlarge the pores and raise the ratio of the pore diameter and the interpore distance without exception ⁽²⁰⁾. According to computerized metallurgical optical microscope technique (CMOMT) images of samples anodized in different types of ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and (H_3PO_4) electrolytes at the maximum film thickness conditions, the ratio of the pore diameter and the interpore distance of anodic film can be seen that in the order:

Phosphoric acid (H_3PO_4) > Oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)

Characteristics of the barrier anodic film

Figures (11) and (12) demonstrate the surface microstructure computerized metallurgical optical microscope technique (CMOMT) images of the anodic oxides at the maximum conditions of film thickness for each sample in both different types of electrolytes boric acid (H_3BO_3) with 0.3 % borax and tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) with ammonium hydroxide in $\text{pH} = 5$ on aluminum alloy (1060), respectively.

Boric acid (H_3BO_3) and tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) electrolytes are both formed nonporous surface layers appeared due to the effect of barrier-layer electrolytes which have no solvent action on aluminum oxide resulted to form a free of pores barrier layers and some high bulges and deep grooves can be observed on the film surface within the optical microscope test domain (5X) magnification power. This phenomenon may be due to the unstable growth of the film, which causes more defects on the film surface and nonuniform of the electric-field intensity ^(21, 22).

Conclusions

1. The structure and property of the films formed at the low voltage region are different from those of the films formed at the high voltage region.
2. In the range of anodizing potentials from 11 to 15 V, the best hexagonal arrangement of pores is observed at 13 V.
3. The porosity of anodic film thickness was decreased according to film thickness where the higher film thickness gives low porosity vice versa with respect to oxalic acid and phosphoric acid. As for boric acid and tartaric acid just the barrier layer was built.
4. Film thickness can be seen that in the order:
Oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) > Phosphoric acid (H_3PO_4) > Tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) > Boric acid (H_3BO_3)
5. Porosity of anodic film at the maximum conditions of film thickness can be seen that in the order: Phosphoric acid (H_3PO_4) > Oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$)
6. Surface microstructure from computerized metallurgical optical microscope technique (CMOMT) images showed that the ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) coating surface has the best nearly hexagonal arrangement of uniform small diameter microstructure of pores and a large number of fine pores like a sponge, while (H_3PO_4) coating surface consists of a large

diameter of pores in comparison with oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) coating surface. Boric acid (H_3BO_3) and tartaric acid ($C_4H_6O_6$) coatings surfaces consists of a thin coating nonporous microstructure was noticed, barrier layer was built.

References

1. Mott, L., and Robert, P. E., (1996), "**Applied Strength of Materials**", Prentice-Hall Inc.
2. Unterweiser, P.M., and Penzenik, M., (2005), "**Worldwide Guide to Equivalent Nonferrous Metals and Alloys**", first edition, American Society for Metals, p.8.
3. Sulka, G. D., and Eftekhari, E. A., (2008), "**Highly Ordered Anodic Porous Alumina Formation by Self – Organised Anodizing and Template – Assisted Fabrication of Nanostructured Materials**", Nanostructured Materials in Electrochemistry Publications, Wiley-VCH, p.1–116.
4. Sheasby, P. G., and Pinner, R., (2001), "**The Surface Treatment and Finishing of Aluminum and its Alloys**", sixth edition, ASM International and Finishing Publications Ltd., p. 427–596.
5. Alwitt, R.S., (2002), "**Anodizing**", (<http://www.electrochem.cwru.edu/ed/encycl.html>).
6. Henley, V.F., (1982), "**Anodic Oxidation of Aluminum and Its Alloys**", first edition, England, Pergamon Press Ltd., p.60–104.
7. Hubner, W.E. and Schiltknecht, A., (1960), "**The Practical Anodizing of Aluminum** ", first edition, Macdonald and Evans Ltd.
8. Duan, H., Yan, C. and Wang, F., (2007), "**Surface and Coatings Technology**", J. **Electrochim. Acta**, Vol. 52, p.3785.
9. Forno, A. D. and Bestetti, M., (2010), "**Effect of the Electrolytic Solution Composition on the Performance of Micro-Arc Anodic Oxidation Films Formed on AM60B Magnesium Alloy**", Italy, Elsevier, p.1–6.
10. Thompson, G. E., (2000), "**The Effect of Current Density on Anodic Film Growth on Al-Cu Alloy**", Proceeding of 2nd International symposium on aluminum surface science and technology, Manchester, p. 21–186.
11. Sponere, R.C., (1955), J. **Electrochem. Soc.**, Vol. 102, No. 4, p. 156.
12. Tope, N.A., (1963), "**Electroplating and Metal Finishing**", Vol.16, No.7.

13. Frankel, G.S., (2004), "**Localized Corrosion of Metals; A review of the Rate-Controlling Factors in Initiation and Growth**", Fontana Corrosion Center.
14. Birss, V., Xia, S., Yue, R. and Richard, J., (2004), *J. Electrochem. Soc.*, Vol. 151, p.1–10.
15. Heber, K.V., (1978), *J. Electrochim. Acta*, Vol. 23, p.127–133.
16. Monfort, F., Berkani, A., Matykina, E., Skeldon, P., Thompson, G.E., Habazaki, H. and Shimizu, K., (2005), *J. Electrochem. Soc.*, Vol. 152, p.382–387.
17. Sulka, G. D. and Stepniowski, W. J., (2009), "**Structural Features of Self-Organized Nanopore Arrays Formed by Anodization of Aluminum in Oxalic Acid at Relatively High Temperatures**", *J. Electrochim. Acta*, Elsevier, Poland, Vol. 54, p.3683–3691.
18. Ono, S., Wada, C. and Asoh, H., (2003), "**Effect of Formation Voltage on Structure of Anodic Barrier Films Formed on Aluminum**", 13th Meeting of Asian-Pacific Corrosion Control Conference, Japan, Vol.22, p. 1129.
19. Hass, G. and Scott, N. W., (1950), "**On The Structure and Properties of some Metal Oxide Films**", (<http://dx.doi.org/10.1051/jphysrad:01950001107039400>), Vol.11, No.7, p. 394 – 402.
20. Zhao, N. and Jiang, X., (2007), "**Effects of Anodizing Conditions on Anodic Alumina Structure**", *J. Mater. Sci.*, Springer Science, China, No.2, p.3878–3882.
21. Masuda, K. and Fukuda, P., (1995), "**Ordered metal nanohole arrays made by a two-step replication of honeycomb structure of anodic alumina**", *J. Science*, Vol. 268, p. 466 – 468.
22. Masuda, H., Yamada, H. and Satoh, M., (1997), "**Highly ordered nanochannel array architecture in anodic alumina**", *J. Applied Physical Letters*, Vol. 71, p. 2770–2772.

Table 1. The analysis of aluminum alloy (1060) (wt. %).

Al	Si	Cu	Mn	Mg	Zn	Ti	Fe	V	each others
99.60 min	0.25	0.05	0.03	0.03	0.05	0.03	0.35	0.05	0.03

Table 2. Compositions and concentrations of anodizing electrolytes at different times and constant voltage 13 V.

Process No.	Composition of electrolytes	maximum film thickness, (μm)
1	oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) 10 wt %	14.571
2	oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) 20 wt %	5.597
3	phosphoric acid (H_3PO_4) 10 wt %	8.381
4	phosphoric acid (H_3PO_4) 20 wt %	5.879
5	boric acid (H_3BO_3) 10 wt % with 0.3 % borax	0.493
6	boric acid (H_3BO_3) 20 wt % with 0.3 % borax	0.242
7	tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) 10 wt % with ammonium hydroxide in pH = 5	0.672
8	tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) 20 wt % with ammonium hydroxide in pH = 5	0.317

Table 3. Compositions and concentrations of anodizing electrolytes at different voltages and constant time 30 min.

Process No.	Composition of electrolytes	maximum film thickness, (μm)
1	oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) 10 wt %	8.631
2	oxalic acid ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) 20 wt %	4.991
3	phosphoric acid (H_3PO_4) 10 wt %	7.917
4	phosphoric acid (H_3PO_4) 20 wt %	5.402
5	boric acid (H_3BO_3) 10 wt % with 0.3 % borax	0.423
6	boric acid (H_3BO_3) 20 wt % with 0.3 % borax	0.232
7	tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) 10 wt % with ammonium hydroxide in pH = 5	0.594

8	tartaric acid ($C_4H_6O_6$) 20 wt % with ammonium hydroxide in pH = 5	0.165
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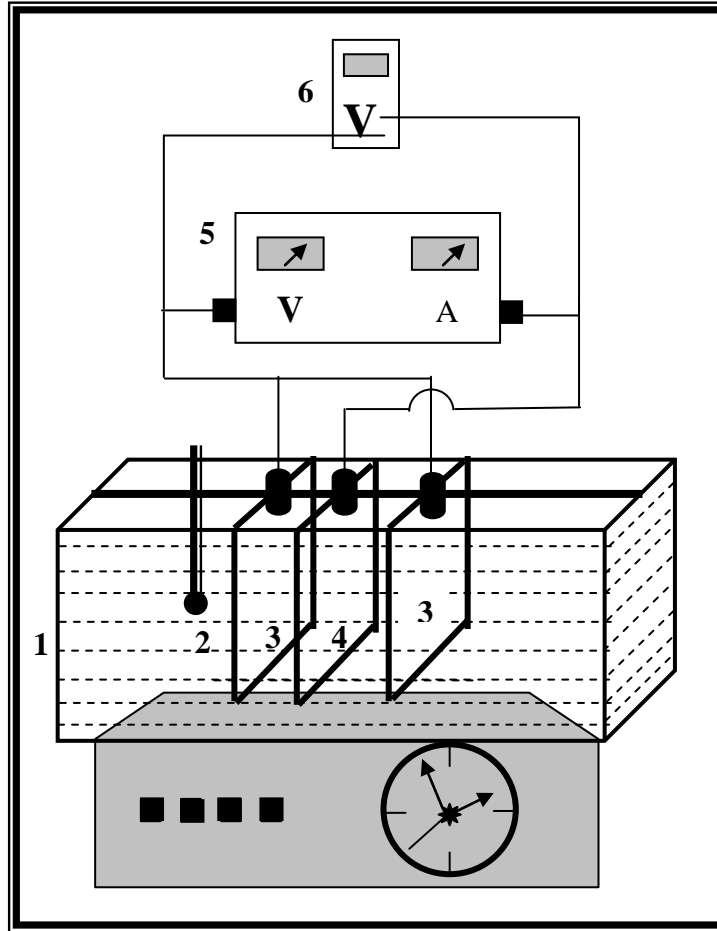


Fig.1 Schematic diagram for the electrochemical system for anodizing work

No.	Item.	No.	Item.
1	Anodizing Cell	4	Anode
2	Thermometer	5	D.C. power supply
3	Cathode	6	Voltmeter

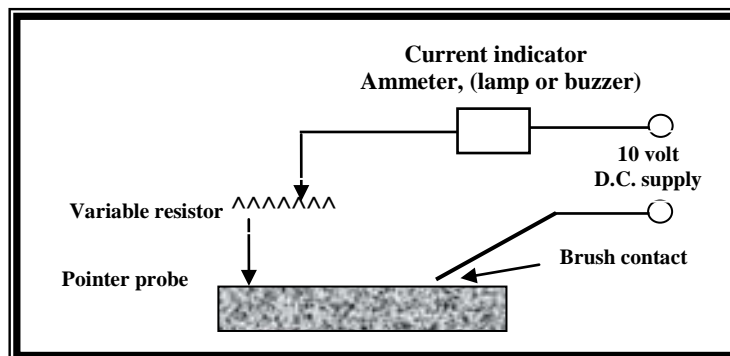


Fig. 2 Equipment used in electrical test for anodic coating

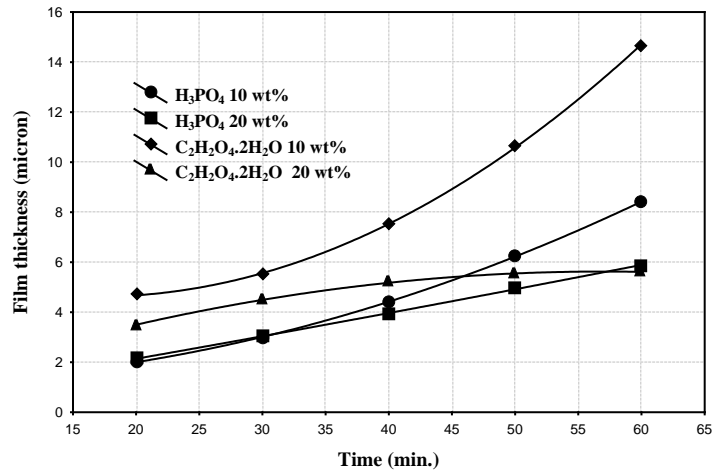


Fig.3 Effect of anodizing time on film thickness in 10 and 20 wt % for oxalic acid and phosphoric acid electrolytes at constant voltage 13V.

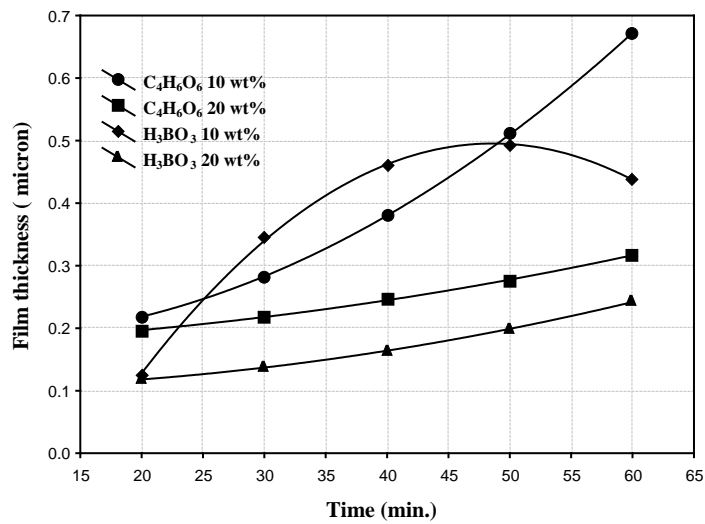


Fig.4 Effect of anodizing time on film thickness in 10 and 20 wt % for

boric acid and tartaric acid electrolytes at constant voltage 13V.

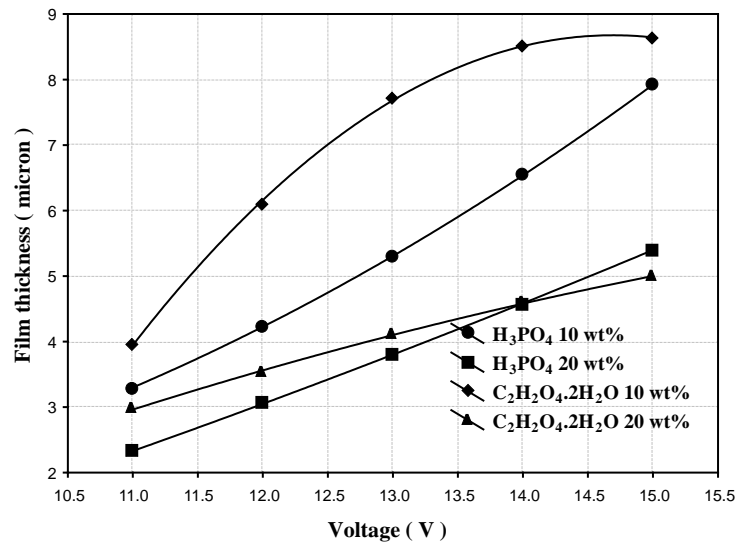


Fig.5 Effect of anodizing voltage on film thickness in 10 and 20 wt % for oxalic acid and phosphoric acid electrolytes at constant time 30 min.

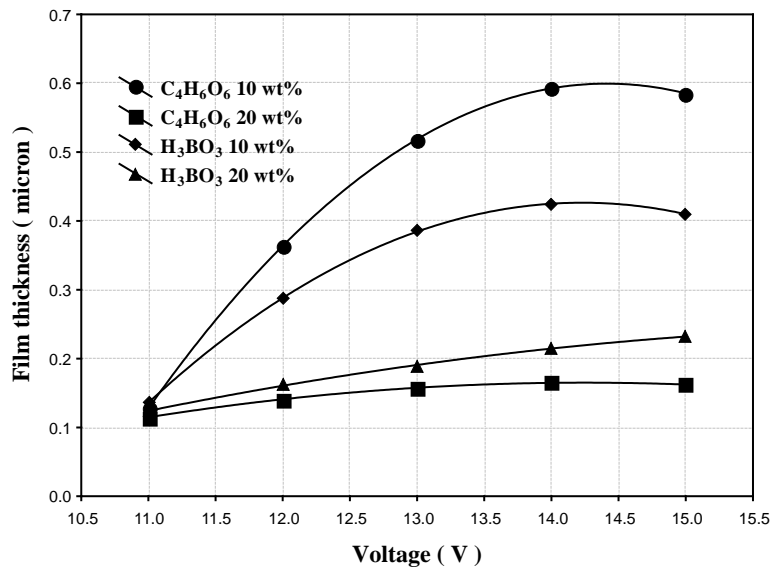


Fig.6 Effect of anodizing voltage on film thickness in 10 and 20 wt % for

boric acid and tartaric acid electrolytes at constant time 30 min.

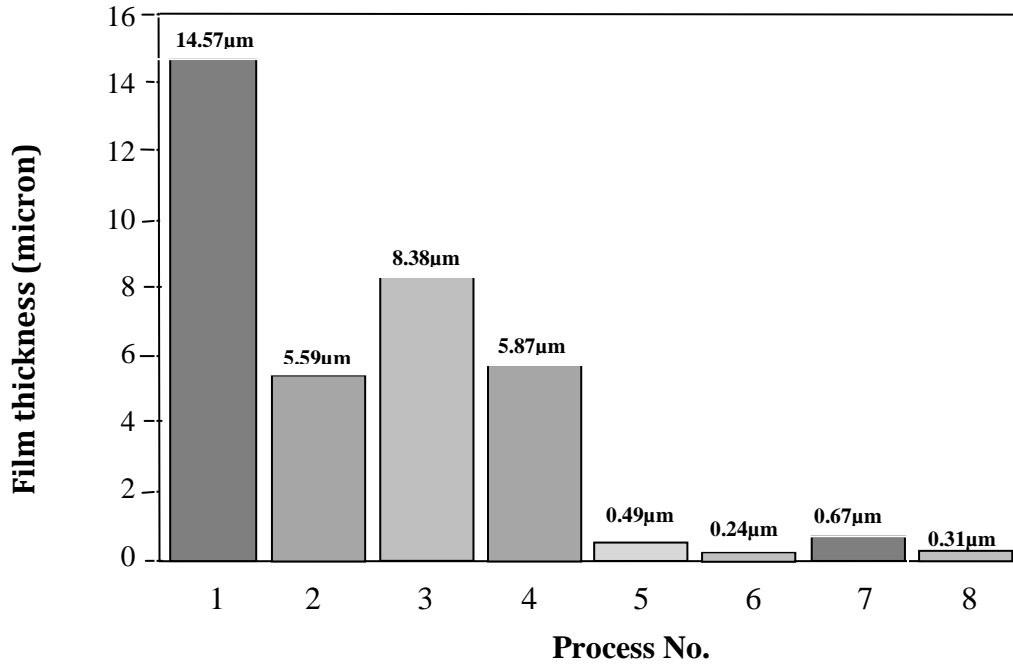


Fig.7 Film thickness formed by different anodizing processes at different times and constant voltage 13 V.

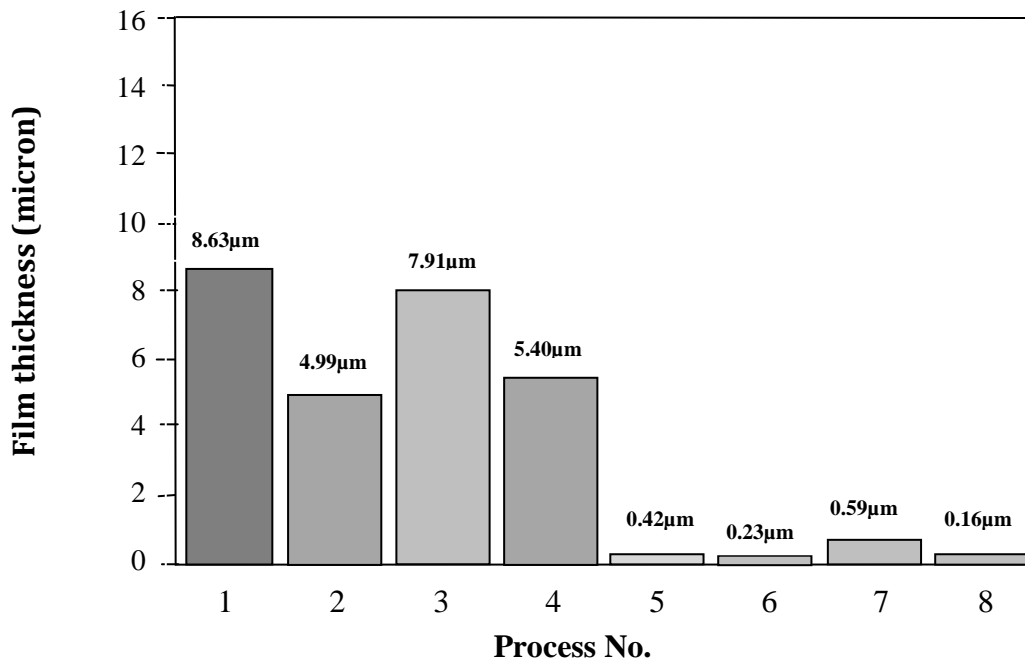


Fig.8 Film thickness formed by different anodizing processes

at different voltages and constant time 30 min.

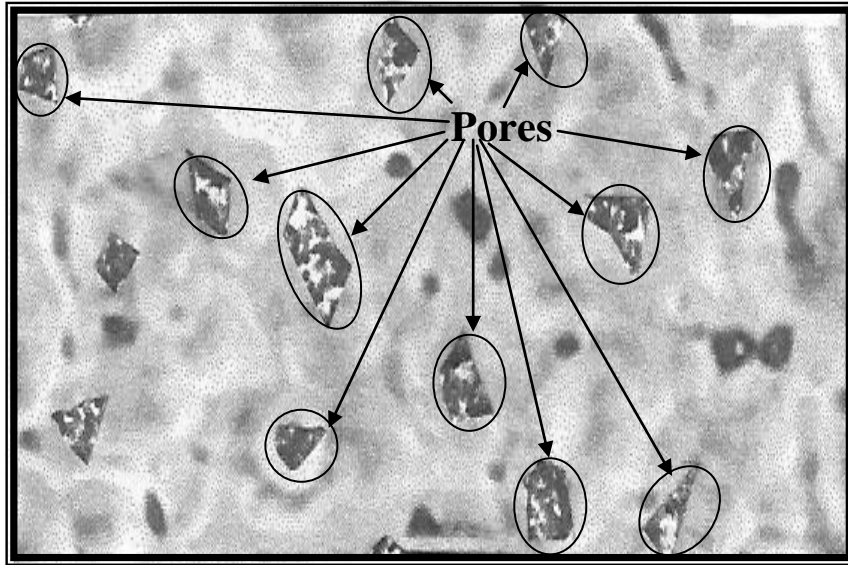


Fig.9 Surface microstructure of porous anodic alumina at the maximum conditions (10 wt % oxalic acid, time 60 min. and voltage 13 V).

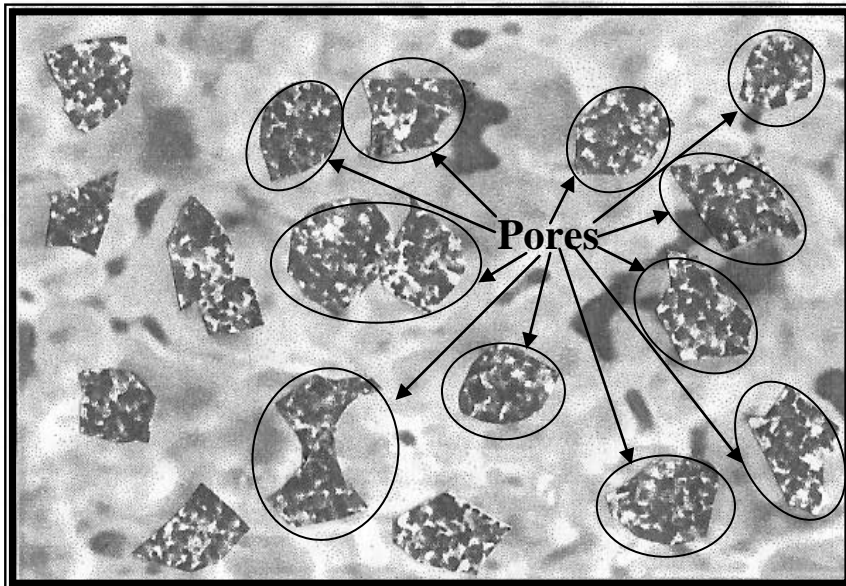


Fig.10 Surface microstructure of porous anodic alumina at the maximum conditions (10 wt % phosphoric acid, time 60 min. and voltage 13 V).

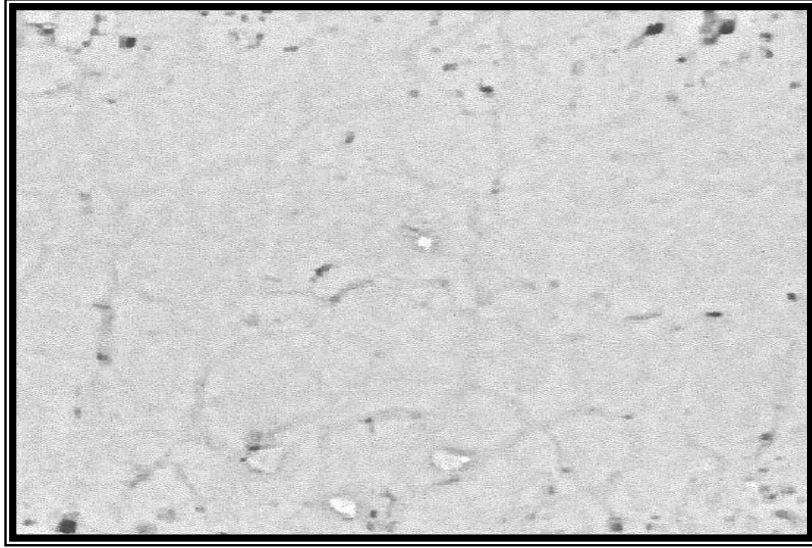


Fig.11 Surface microstructure of barrier anodic alumina at the maximum conditions (10 wt % boric acid, time 50 min. and voltage 13 V).

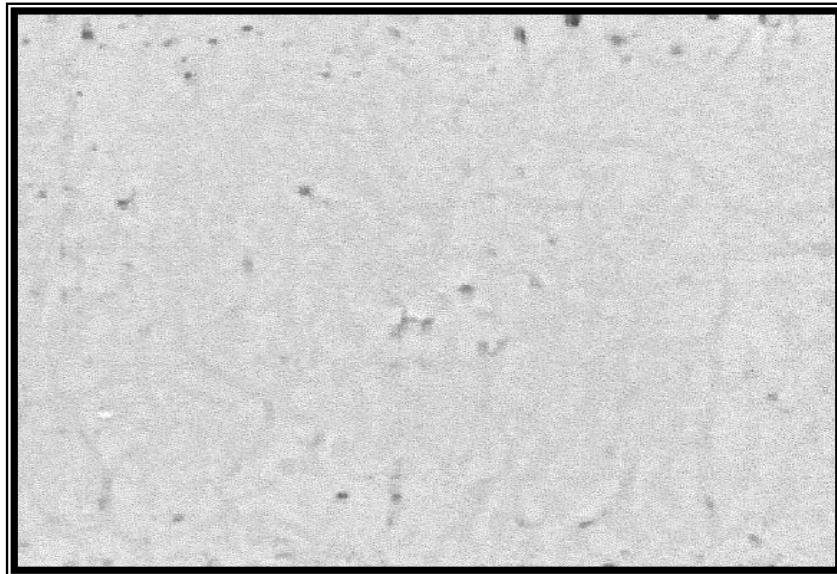


Fig.12 Surface microstructure of barrier anodic alumina at the maximum conditions

(10 wt % tartaric acid, time 60 min. and voltage 13 V).

دراسة مقارنة لأنودة سبيكة المنيوم 1060 بواسطة

انواع مختلفة من المحاليل الأليكتروليتيية

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الخلاصة

الخصائص الأنودية لسبيكة الألمنيوم (1060) تم دراستها بأستخدام أنواع مختلفة من المحاليل الأليكتروليتيية حامض الأوكزاليك ($C_2H_2O_4 \cdot 2H_2O$) ، حامض الفوسفوريك (H_3PO_4) ، حامض البوريك (H_3BO_3) و حامض الترتريك ($C_4H_6O_6$).

تم دراسة تأثير ثلاث متغيرات لبيان تأثيرها على سمك هذه الطبقة. هذه المتغيرات هي : تركيز المحلول يتراوح بين (10-20 % وزنا) ، جهد يتراوح بين (11 - 15 فولت) و زمن الأنودة بين (20 - 60 دقيقة) . درجة الحرارة للخلية الكهروكيمياوية ثابتة عند 27 ° م .

وبينت النتائج العملية أن سمك طبقة الأنودة تأثر بتواكيز المحاليل الحامضية الأليكتروليتيية المختلفة ، جهد الأنودة وزمن الأنودة تبعاً لتأثير كل محلول اليكتروليتيي .

أظهرت النتائج بأن سمك الطبقة الأنودية يزداد مع زيادة زمن و جهد الأنودة وتناقص مع زيادة تركيز الحامض . وأن سمك طبقة الأنودة يزداد لحد أقصى في 60 دقيقة في حامض الأوكزاليك ($C_2H_2O_4 \cdot 2H_2O$) 10 % وزنا ، حامض الفوسفوريك (H_3PO_4) 10 % وزنا و حامض الترتريك ($C_4H_6O_6$) 10 % وزنا على الترتيب . أما بالنسبة لمحلول حامض البوريك (H_3BO_3) 10 % وزنا مع 0.3 % بوراكس يزداد سمك الطبقة لحد أقصى في 50 دقيقة و بعد هذا الزمن حصل التناقص تدريجياً في سمك الطبقة .

أستخدمت تقنية المجهر البصري المعدني المربوط بالحاسبة (CMOMT) عند الظروف القصوى لسمك الطبقة لكل نموذج لتحديد التركيب المجهري لسطح الأوكسيد الأنودي المتكون . وجد أن نوع المحلول الأليكتروليتيي له تأثير على الخصائص الأنودية والتركيب المجهري لطبقة الأوكسيد لسبيكة الألمنيوم (1060).

بينت الدراسة بأن مسامية الطبقة الأنودية تناقصت تبعاً الى سمك الطبقة حيث أن سمك الطبقة الأعلى يعطي مسامية واطئة والعكس بالعكس بالنسبة لحامض الأوكزاليك و حامض الفوسفوريك . أما بالنسبة لحامض البوريك و حامض الترتريك فقد بنيت الطبقة الحاجزة فقط .

الكلمات الدالة: سبيكة المنيوم (1060) ، أنودة ، أنواع أليكتروليتيات مختلفة ، حامض الأوكزاليك ، حامض الفوسفوريك ، حامض البوريك ، حامض الترتريك ، بوراكس ، أوكسيد أنودي

