Characterization of Porous Anodic Aluminium Oxide Film on Aluminium Templates Formed in Anodizing Process

Juyana A.Wahab and Mohd. Nazree Derman

Abstract**—**A porous anodic aluminium oxide (AAO) films were successfully fabricated on aluminium templates by using anodizing technique. The anodizing process was done in the mixed acid solution of phosphoric acid and acetic acid. The growth, morphology and chemical composition of AAO film were investigated. During the anodizing process, the growth of the oxide pores was strictly influenced by the anodizing parameters. The anodizing was done by varying the voltage at 70V to 130V and temperature from 5°C to 25°C. The electrolyte concentration was remaining constant. In this study, all the samples were characterized using scanning electron microscope (SEM) and X-ray diffraction (XRD) techniques. From this study, the optimum parameters to obtain porous AAO film with the mixture of phosphoric acid and acetic acid solution can be known.

Keywords**:** Anodizing, Anodic Aluminium Oxide, Mixed Acid, Pore Growth, Voltage, Temperature

I. INTRODUCTION

Anodic aluminium oxide (AAO) film can be grown in the mixed solution of phosphoric acid and acetic acid (H_3PO_4+CH_3COOH) solution. AAO film can be generated from a highly pure aluminium substrate by anodizing process. The AAO film that is formed on an aluminium substrate has straight and uniform nanopores that form a hexagonal structure. The AAO can be used in the manufacturing of hard disc, adhesives, templates for nanoparticles, magnetic materials, photocatalysis and also prepare ordered or patterned nanostructure arrays.

Anodizing process has been developed for aluminium, stainless steel, titanium and also magnesium. However, aluminium anodizing has been widely studied because aluminium always covered with a thin oxide film because of the high affinity for oxygen which makes the aluminium an excellent corrosion resistant metal [1, 2]. Aluminium is widely used in electronics because of the high strength-to-weight ratio, high thermal conductivity and good electrical conductivity. Anodizing of aluminium has raised scientific and technological interest due to the diverse applications which include dielectric film production for use in electrolytic capacitors, sensors fabrication, increasing the oxidation resistance, abrasion resistance, corrosion resistance and wear resistance of materials [3].

In this study, the mixed solution of H_3PO_4+CH_3COOH was used to create the AAO film with controlled morphology. This mixed solution as anodizing electrolytes can decrease the film dissolution rate and then increase the film formation efficiency and improve the film properties. However, optimum parameter which need for this process is very difficult to achieve because the behaviours of the porous AAO film properties strictly influenced by anodizing process parameter such as anodizing voltage, electrolyte temperature, acid concentration and duration of anodizing process.

The study approach on anodizing process will be explored by using H_3PO_4+CH_3COOH to obtain the nanostructured porous AAO film on aluminium substrate. Thus, the new hypothesis will be generated with explore the relationship between anodizing parameters and substrate properties on nanostructured AAO film in microstructural and chemical properties in order to enlarge its usage especially in electronic applications.

II. EXPERIMENTAL

The fabrication of aluminium substrate was done by melting and casting process. In this experiment, pure aluminium pellets (99%) were melted in a graphite crucible in induction furnace under vacuum atmosphere at temperature 850°C. The melt was cast into stainless steel 304 mould (Ǿ 20 mm) and cooled in open air at room temperature. The 3mm thickness sample was grinded and then polished using 6µm and 1µm diamond paste to obtain mirror like surface. The anodizing process

Juyana A.Wahab. Author is with the School of Materials Engineering, Universiti Malaysia Perlis, Perlis, Malaysia. (phone: +60129259776; fax: +604-9798178; e-mail: juyana1506@yahoo.com).

Mohd Nazree Derman. Author is with Institute of Nano Electronic Engineering, Universiti Malaysia Perlis, Perlis, Malaysia. (e-mail: nazree@unimap.edu.my).

was used mixed phosphoric acid and acetic acid as electrolytes. This anodizing process was done at 70V-130V at temperature 5°C to 25°C for 60 minutes. The sample was characterized by using scanning electron microscope (SEM) model JEOL JSM-6460LA SEM and x-ray diffraction spectroscopy (XRD) model XRD-6000 Shimadzu.

III. RESULTS AND DISCUSSIONS

AAO Pore diameter

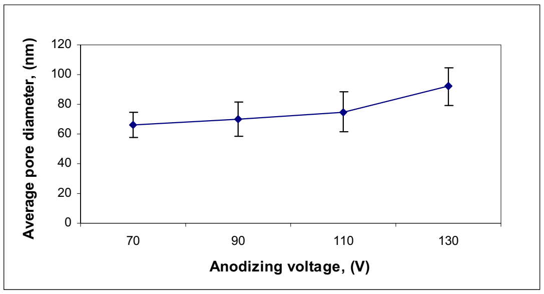

Figure 1: Effect of anodizing voltage on average pore diameter of AAO film.

In this study, the aluminium substrates were anodized in different anodizing voltage from 70V to 130V. The results show that the average pore diameter is gradually increase by increasing the anodizing voltage as shown in figure 1. At 70V, the average pore diameter of AAO film is about 66nm. The pores are irregular and smaller. The pore diameter is increase to 70nm when the anodizing voltage is increase to 90V. The pore diameter is continually increased to 75nm and 92nm as the anodizing voltage is set to 110V and 130V. The largest pore diameter is shown in highest applied voltage which at 130V. The formation of AAO porous structure on the surface of AAO film is due to the dissolution of oxide layer. Reference [4] have been reported that the rate of dissolution of oxide layer increase with applied anodizing voltage. At high applied anodizing voltage, there is a high degree of hydration and ion incorporation and thus dissolution of oxide layer is at highest rate. Thus, the diameter of pore increased. The decrease in hydration and anion incorporation in the electrolyte cause lower dissolution rate of oxide layer and cause the decreasing of pore diameter.

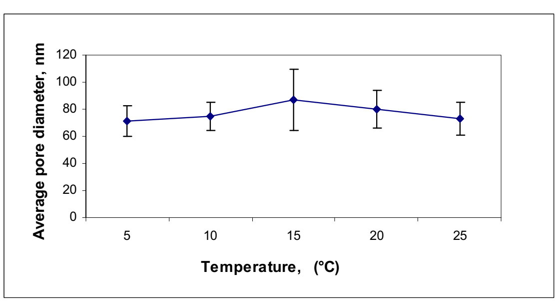

Figure 2: Effect of anodizing temperature on average pore diameter of AAO film.

Besides, the anodizing temperature is affected to the formation of AAO film. The results show that small pore diameter will be obtained when AAO film anodized at low temperature which is at 5°C to 10°C. Largest pore diameter is obtained at 15°C and the pore diameter become smaller at 20°C to 25°C. Figure 2 shows the effect of anodizing temperature on average pore diameter of AAO film. This result is supported by [5]. According to [5], AAO film anodized at higher temperature led to the small pore diameter. In the study, the anodizing process is conducted in 0.4M H_3PO_4 with current density of $35mA^{-2}$. The results show that at 35°C, the AAO pore diameter is about 50nm and this value is increase to 100nm and 170nm when the temperature is decrease to 25°C and 15°C. Reference [6] told that anodizing temperature is suitable to be kept below the room temperature. This is the cause of high anodizing temperature enhance the dissolution of porous oxide film in the electrolyte. High rate of dissolution of oxide layer caused the pore diameter become larger.

SEM Micrographs and Thickness of AAO Film

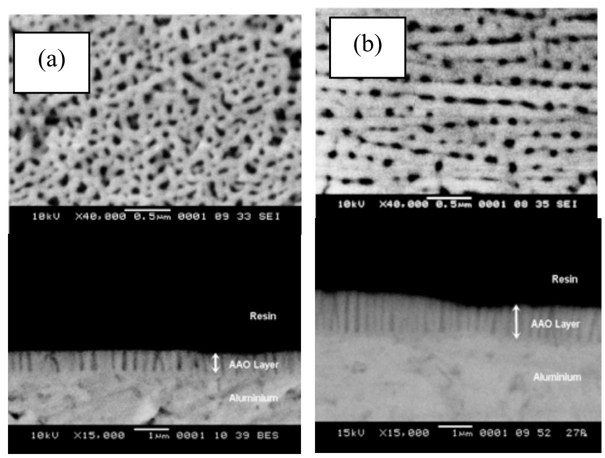

Figure 3: Surface morphology and thickness of anodized AAO in H_3PO_4+CH_3COOH electrolyte anodized with temperature 15°C at voltage (a) 70V and (b) 110V.

The rate of the oxide films is expressed as the film thickness formed in anodizing process. In this study, the thickness of AAO film is measured by using SEM micrographs cross sectional of the film. Figure 3 shows SEM micrographs of AAO film and cross sectional for different anodizing voltage.

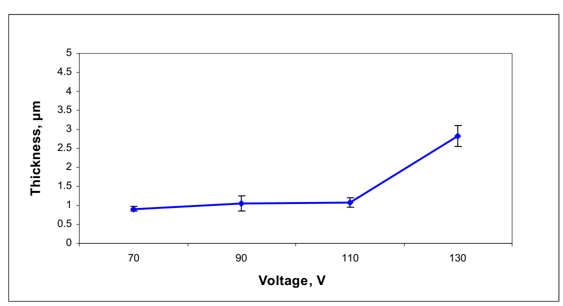

Figure 4: The effect of anodizing voltage to the thickness of AAO film.

The observation through the SEM micrographs shows that the thickness of AAO film is increase as the anodizing voltage increase. The effect of anodizing voltage to the thickness of AAO film is shown in figure 4. Refer to [7], the thickness of AAO film increase as the anodizing voltage increase when the anodizing process is conducted in 4wt% H_3PO_4. This is the cause of the higher the applied voltage in anodizing process resulted to the increment of the solvent action of electrolyte. This result also supported by [8] which has been studied the effect of anodizing voltage on the formation of AAO film. The anodizing process is done in 4% H_3PO_4 at 20°C of anodizing temperature. The behaviour of ions in the electrolyte is dependent with applied voltage. At low anodizing voltage, the surface of oxide layer has negatively charge and caused the amount of oxygen ions in the electrolyte reduced. Therefore, the rate of oxide formation is low. Besides, anodizing above 38V of anodizing voltage caused the protons or H_3O^+ ions injected from electrolyte into the oxide layer. The amount of protons or H_3O^+ ions injected into oxide layer increase with the anodizing voltage and resulted to greater thickness of the oxide layer [9].

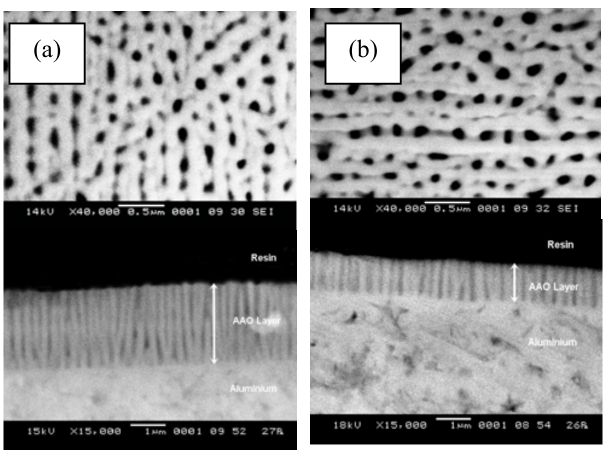

Figure 5: Surface morphology and thickness of anodized AAO in H_3PO_4+CH_3COOH electrolyte anodized with 130V at temperature (a) 15°C (b) 20°C.

The formation of oxide film on aluminium surface occurs by the contribution of ions in the electrolyte. The existence and behaviour of the ions in the electrolyte is depends on the electrolyte temperature. Figure 5 shows the effect of anodizing temperature on surface morphology and thickness of anodized AAO film. At temperature 5°C and 10°C, the percentage of mass change and the thickness of AAO film is decreased. At low temperature, the rate of ions transfer in the electrolyte is low. Therefore, the rate of oxide formation becomes low. The optimum anodizing temperature that suitable with this type of electrolyte is 15°C. At this temperature, the ions are efficiently transport in the electrolyte and cause the formation rate of oxide is high. The ions generation is also at high rate at this temperature. This is shown by the highest percentage of mass change and thickness of AAO film at 15°C temperature. For temperature 20°C to 25°C, the rate of ions transport is decrease compared to temperature 15°C. The rate of ions generation and the ions behaviour become slow at temperature 20°C to 25°C and resulted to low rate of AAO film formation. Figure 6 shows the effect of anodizing temperature to the thickness of AAO film.

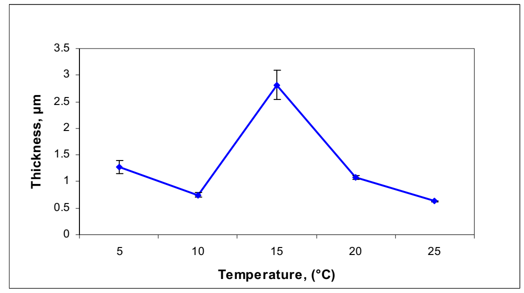

Figure 6: The effect of anodizing temperature to the thickness of AAO film.

This result is similar with [10] which has been reported that an increase in temperature resulted to an increase in the growth rate of AAO film formed in phosphoric acid electrolyte. At temperature 20°C to 25°C, the mass of oxide film increase but the mass of oxide film decrease when the temperature increase to 30°C. The effect of temperature on the formation of AAO film is obvious because the anodizing temperature affects the rate of ion transport across the oxide layer, the oxide dissolution from the pore wall and heat transport rates within the pore and the electrolyte.

XRD Analysis

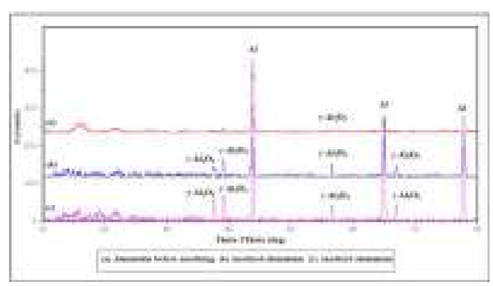

Figure 7: XRD analysis of aluminium substrate before and after anodizing process.

Figure 7 shows the diffraction peak of anodized sample in the H_3PO_4+CH_3COOH solution. From the diffraction pattern of the sample, aluminium and aluminium oxide phase was existed in the anodized sample. Therefore, there was aluminium oxide layer formed on the aluminium substrate surface in the anodizing process. The aluminium peak is existed at angle 2θ = 44.73°, 65.13° and 78.23° (JCPDS#04-0787) as shown in figure 7(a). However, in this study γ-aluminium oxide (γ-Al_2O_3) was formed on the substrate surface. For figure 7(b), the peak is shown at angle around 2θ = 37.52° (JCPDS#50-0741), 39.29° (JCPDS#50-0741), 56.89° (JCPDS#50-0741) and 67.26° (JCPDS#10-0425). For figure 7(C), the peak existed at angle around 37.56° (JCPDS#50-0741), 39.28° (JCPDS#50-0741), 56.76° (JCPDS#50-0741) and 67.11° (JCPDS#10-0425).

IV. CONCLUSION

Porous AAO film was successfully fabricated in the solution of H_3PO_4+CH_3COOH. The result of surface morphology, chemical composition and the formation rate of AAO film were obtained. Higher anodizing voltage at 130V led to the larger pore diameter which is around 92nm and the pores were uniformly distributed on the substrate surface. Besides, the anodizing temperature is suitable to be in the range of 10°C to 20°C. The XRD diffraction pattern shows the existence peaks of γ-Al_2O_3 that formed in the anodizing process. From this research, the optimum parameters to obtain nanoporous AAO thin film with solution of H_3PO_4+CH_3COOH can be known. The anodizing voltage should be in the range of 70V – 130V and the optimum anodizing temperature is about 15°C in order to produce ordered arrangement of pores below 100 nm in size.

REFERENCES

[1] S. K. Hwang, S. H. Jeong, H.-Y. Hwang, O.-J. Lee, and K.-H. Lee, "Fabrication of Highly Ordered Pore Array in Anodic Aluminium Oxide," *Korean J. Chem. Eng.,* vol. 19, pp. 467-473, 2002.

[2] C. Rajagopal and K. I. Vasu, *Conversion Coatings A Reference for Phosphating, Chromating and Anodizing Processes*. New Delhi: McGraw-Hill 2000.

[3] A. Eftekhari, "Nanostructured Materials in Electrochemistry," in *Highly Ordered Anodic Porous Alumina Formation by Self-Organized Anodizing*, G. D. Sulka, Ed. Weinheim: Wiley-VCH, 2008.

[4] A. A. Mazhar, F. E.-T. Heakal, and K. M. Awad, "Some formation factors affecting the dissolution behaviour of anodic oxide films on aluminum in H3PO4," *Thin Solid Films,* vol. 192, pp. 193-199, 1990.

[5] J. D. Laet, H. Terryn, and J. Vereecken, "Development of an optical model for steady state porous anodic films on aluminium formed in phosphoric acid," *Thin Solid Films,* vol. 320, pp. 241-252, 1998.

[6] J. Sarkar, G. G. Khan, and A. Basumallick, "Nanowires: Properties, applications and synthesis via porous anodic aluminium oxide template," *Bulletin of Materials Science,* vol. 30, pp. 271-290, 2007.

[7] M.-R. Yang and S. K. Wu, "The improvement of high-temperature oxidation of Ti-50Al by anodic coating in the phosphoric acid," *Acta Materialia,* vol. 50, pp. 691-701, 2002.

[8] I. Vrublevsky, V. Parkoun, and J. Schreckenbach, "Analysis of porous oxide film growth on aluminum in phosphoric acid using re-anodizing technique," *Applied Surface Science,* vol. 242, pp. 333-338, 2005.

[9] I. Vrublevsky, V. Parkoun, J. Schreckenbach, and W. A. Goedel, "Dissolution behaviour of the barrier layer of porous oxide films on aluminum formed in phosphoric acid studied by a re-anodizing technique," *Applied Surface Science,* vol. 252, pp. 5100-5108, 2006.

[10] A. T. Shawaqfeh, "Fabrication and Characterization of Novel Anodic Alumina Membranes," in *Chemical Engineering*. vol. deg. of Doctor of Philosophy New York: Clarkson University, 1997.