

VOLTAGE EFFECT ON ELECTROCHEMICAL ANODIZATION OF ALUMINUM AT AMBIENT TEMPERATURE

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ABSTRACT

The effect of voltage on nano pores formed via electrochemical anodization of high purity Aluminum was investigated. The electrochemical bath consists of phosphoric acid electrolyte; a platinum electrode was used as the cathode electrode, and aluminum template as anode electrode. The anodization process was carried out at ambient temperature with voltage range of 20V to 80V, which is the voltage range achievable by the in house electrochemical cell. It is observed after the anodization process that there is slight phase change in the aluminum substrate of its FCC structure to Monoclinic at 39° and 45° with the same effect for all the applied potentials; secondly it was also observed that at every voltage increment there is a significant increase in current density, as well as increase in the nano pore size from about 40nm to 300nm. The morphology and phase composition were characterized by scanning electron microscope (SEM), energy dispersive spectroscopy (EDX), X-ray diffraction and Voltage time graph.

Keywords: Aluminum; Ambient temperature; Electrochemical; Electrolyte; Nano pores

1. INTRODUCTION

Porous alumina, which is formed by anodizing high-purity aluminum in an appropriate acid solution, has been studied extensively over the last five decades (Feng & Adrian 2008). Nanoporous anodic alumina films have attracted a great scientific and technological interest (Marsal et al. 2009) as a material for nanotechnology applications because of their unusual properties compared to the bulk counterparts (Feng et al. 2009.)

Among the simplest, cheapest and most straight-forward approaches that lead to ordered nanostructures are anodization techniques. The best explored case is Al and the growth of self-ordered porous alumina layers (Macak et al. 2007). The synthesis and anodization of aluminum to produce nanoporous alumina have been reported from alkaline sodium phosphate (Araoyinbo et al. 2009); oxalic acid (Hou et al. 2002), (Li & Huang 2007), (Su et al. 2008);

sulfuric acid (Sulka et al. 2002), (Azevedo et al. 2004), (Belwalkar et al. 2008), (Sulka & Parkola 2007), (Kang et al. 2007); phosphoric acid (Chu et al. 2003), (Araoyinbo et al. 2009), (Wang et al. 2008); and neutral electrolyte (Araoyinbo et al. 2010). Most of the reported work, used phosphoric acid electrolyte with the aid of temperature controlled water bath to anodize the aluminum template at low temperatures (i.e. 10°C, 20°C) and in some cases extremely low temperatures (i.e. 0°C, 1°C, 2°C etc) with the exception of Araoyinbo et al.

In this paper, anodized aluminum of different pore size with every voltage increment in phosphoric acid electrolyte at ambient temperature has been investigated. A schematic diagram of the electrochemical cell set up for the anodization process is shown in fig1. It is known that pore formation during anodization process varies with the electrolyte type, concentration, temperature, and applied anodization potential (Proenca et al. 2008). The results we obtained, shows the direct relationship between the applied voltage and the current density which plays a key role in producing different diameters of the porous structure.

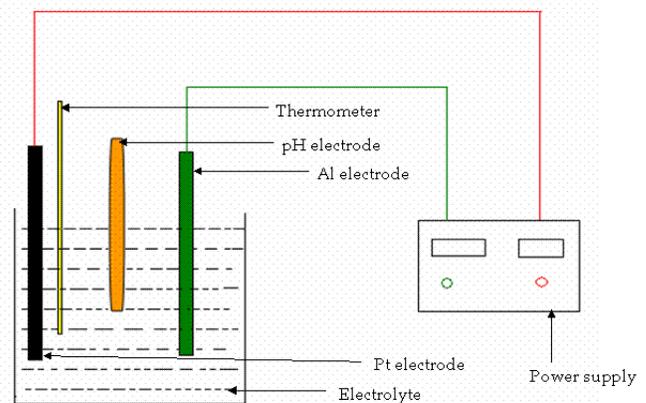


Figure.1 Electrochemical cell

2. EXPERIMENTAL

High purity aluminum (99.3%, 0.3mm thick) was used as the template in the phosphoric acid electrolyte. The aluminum template was purged by acetone in ultrasonic cleaner to clean out possible grease on its surface (Zhu et al. 2005). Before anodizing, electrochemical polishing of

samples was carried out in a 1:4 volume mixture of HClO_4 and $\text{C}_2\text{H}_5\text{OH}$ at constant current density of 500mAcm^{-2} for 1min at 10°C . (Grzegorz & Wojciech 2009). The samples were later rinsed with distilled water, and a single-walled electrochemical cell with a magnetic stirrer (500 r.p.m.) was used to anodize the samples in 20% phosphoric acid electrolyte, for 1 & 3hours within voltage range of 20 to 80 V at ambient temperature. Pt electrode served as the cathode electrode and the distance from the aluminum anode electrode was 3.5cm.

A Bruker D8 Advance X ray diffractometer with Cu target was used to obtain the X-ray diffraction patterns of the samples, and the surface microstructure of the anodized aluminum films was observed using scanning electron microscope (SEM) Model Supra 35VP and EDX (EDAX).

3. RESULTS AND DISCUSSIONS

Morphology

The morphology of the anodized aluminum porous films was examined by scanning electron microscopy (SEM). Fig.2 shows the FE-SEM images of the anodized aluminum structure.

Fig.2 (a) and (b) illustrates that the top view of the pores formed is distributed continuously with tiny round pores as a result of the low voltage. The pore size for fig.2 (a) & (b) is in the range of 40-70nm with mean size of 55nm and a current density range of 2A/cm^2 - 4A/cm^2 .

Fig. 3 (a) and (b) under a 40V applied potential shows the randomly distributed nano pores distributed all over the surface of the template because of the one step anodization process used. The pore size is in the range of 60-130nm with mean size of 95nm and a current density range of 4A/cm^2 - 6A/cm^2 .

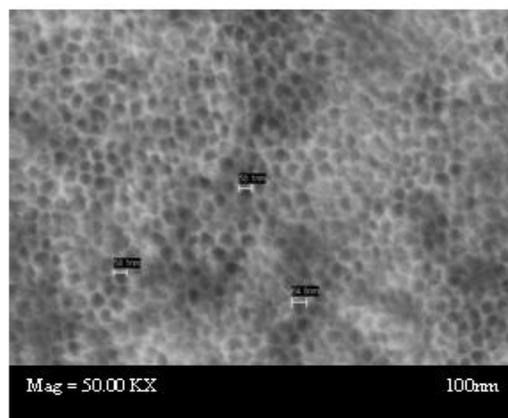
Fig. 4 (a) and (b) shows SEM image of applied potential of 60V much higher than the previous two and have its pores randomly distributed all over the material surface with pore size in the range of 80-170nm with mean size of 125nm and current density range of 6A/cm^2 - 8A/cm^2 .

Fig. 5 (a) and (b) shows the highest voltage attainable by our set –up, it has pores that are quite bigger compared to the previous four results. The pore size is in the range of 180-300nm with mean size of 240nm and current density of 8A/cm^2 - 10A/cm^2 .

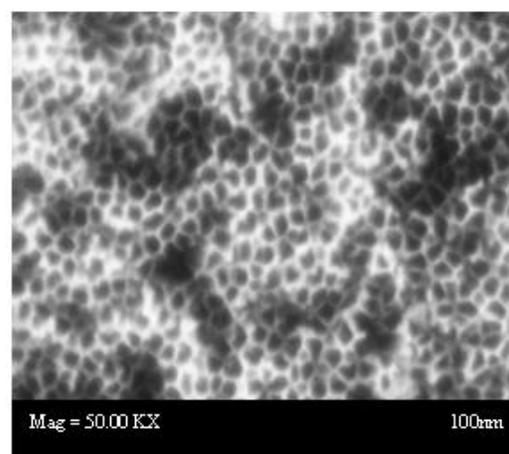
All the FE-SEM micrograph shows the effect of increased voltage on the Al substrate, increasing the voltage increases the current density, and subsequently the pore size of the nano porous alumina produced. The nucleation and growth of this pores indicates that alumina pore size can be controlled.

The increase in pore size was made possible by the following relationship;

$$V \propto I \quad (1)$$

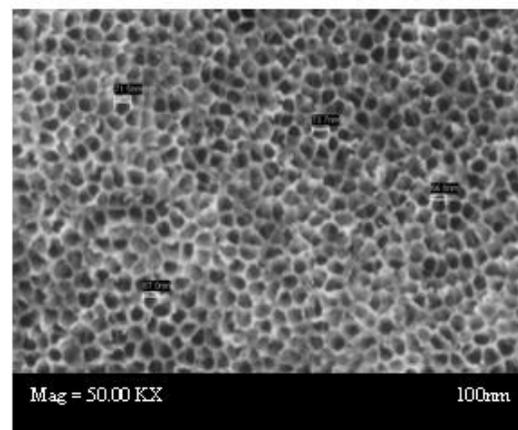


(a) 1hour anodization time

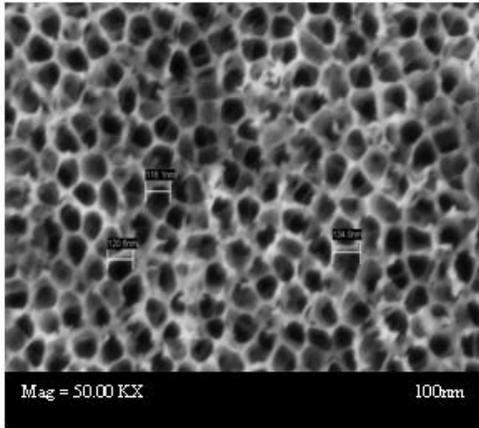


(b) 3hours anodization time

Figure.2 FE-SEM images of the top view of anodized aluminum at 20V



(a) 1hour anodization time



(b) 3hours anodization time

Figure. 3 FE-SEM images of the top view of anodized aluminum at 40V

$$I \propto 1/R \quad (2)$$

Using the relationship between voltage and resistor, the Ohm's law states the current through a conductor between two points is proportional to the potential difference and inversely proportional to the resistance therefore,

$$I = V/R \quad (3)$$

where I is the current in the amperes, V is the potential difference in volts and R is a circuit parameter called the resistance (measures in Ohms which is equivalent to volts per ampere). If the voltage doubles the current flowing in the circuit also doubles.

Current density which is defined as a vector whose magnitude is the electric current per cross-sectional area is shown in equation 4.

$$J = I / A \quad (4)$$

J = current density

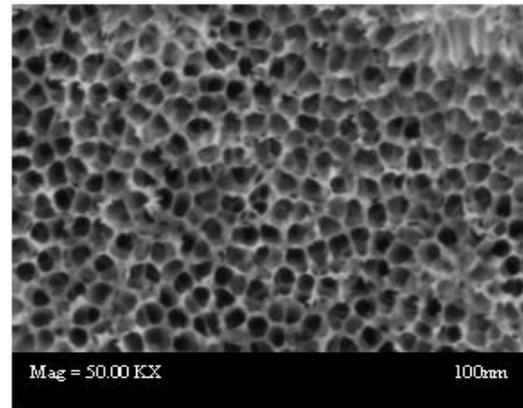
I = applied current

A = cross sectional area of the material.

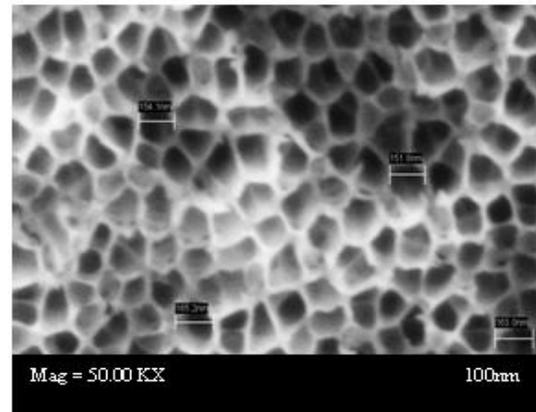
From the above relationship, voltage increment results in significant increase in the current density which increases the rate of chemical dissolution of the oxide layer formed during the anodization process while the cross sectional area of the material remains constant. The effect is visible in the nano pores formed on the aluminum substrate.

The SEM of fig 6 shows the formation of barrier oxide film during initial anodization of the aluminum in the electrolyte. This oxide film is formed as a result of voltage application and subsequent oxidation reaction between the metal and the electrolyte. Prolong anodization leads to dissolution of the oxide film and formation of porous alumina which is shown in fig 7 after 30seconds. Both figures confirm that the oxide film formation at the initial

stage and the emergence of pores proceeds at a fast rate as a result of the voltage application, current density and the acidic nature of the electrolyte.

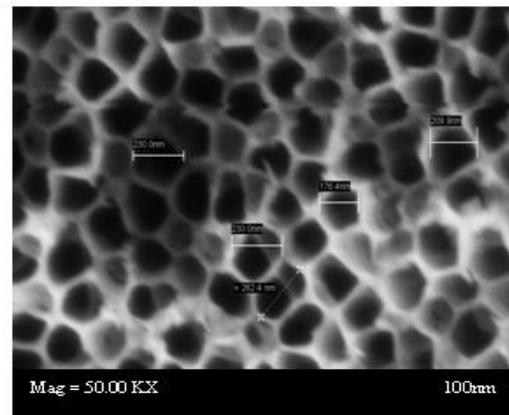


(a) 1hour anodization time

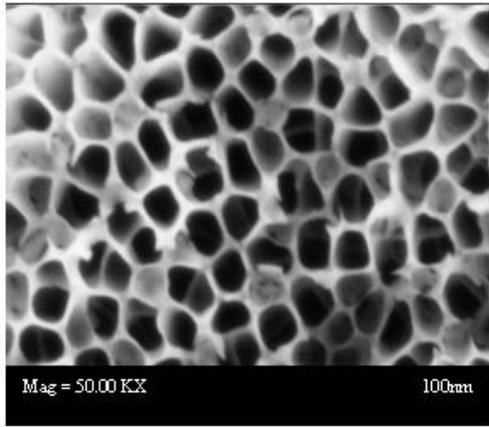


(b) 3hours anodization time

Figure. 4 FE-SEM images of the top view of anodized aluminum at 60V



(a) 1hour anodization time



(b) 3hours anodization time

Figure.5 FE-SEM images of the top view of anodized aluminum at 80V

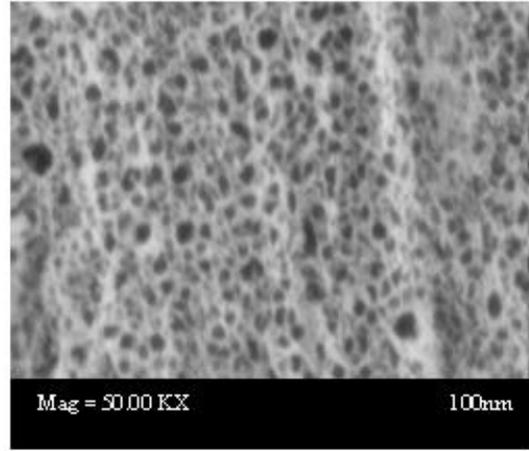


Figure.7 Barrier oxide break down after 30sec

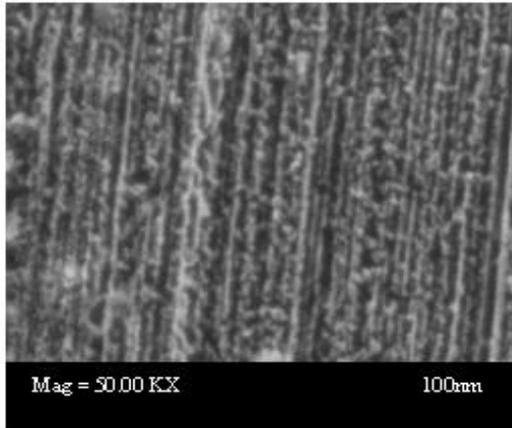


Figure.6 Aluminum oxide barrier film

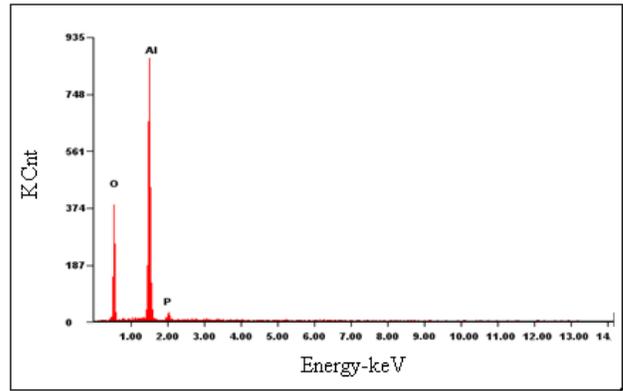


Figure. 8 EDX of anodized aluminum

Figure 8 and table 1 shows the energy dispersive X-ray (EDX) spectrum corresponding to the Al, O and P detected with their elemental compositions. The P peak is still detectable irrespective of the potential applied or duration of the anodization but in a minute amount which is probably due to the difficulty to adsorb on the surface of the oxide films.

Table.1 Elemental composition after anodization from EDX

Element	wt. %	at. %
O	41.08	54.22
Al	55.60	43.51
P	03.32	02.27
Total	100.00	100.00

Structural Characterization

Figure 9 shows the X-ray diffraction spectra of nano pores on anodized aluminum substrate from 20V to 80V; the change in the FCC to Monoclinic structure is noticeable at 111 and 200 plane which corresponds to 39 and 45° on the 2-theta scale. The low broad peak at 39 and 45° might be indicative of amorphous aluminum oxide compound formed. All the applied potentials produce the same phase change result.

Voltage Time Graph

Figure 10 shows the relationship between voltage and time from the plotted graph; the points a, b, c and d represent

the three stages of anodization of aluminum from 20 to 80V with similar curves, the initial stage is shown by segment ab in which aluminum oxide barrier film grows on the aluminum surface as shown in fig6 and within 30sec a break down of the oxide occurs and very tiny pores start to form as shown in fig7; segment bc represents the second stage of the anodization process in which there is field assisted dissolution mechanism of the oxide, then the film electric resistance decreases with the emergence of increasing pores, the anodizing voltage also decreases subsequently with the applied potentials; the segment cd which is the final stage of the anodization shows a steady state voltage reached when the rate of the field dissolution of the alumina at the base of the pores equals the oxide formation rate at the metal-oxide interface.

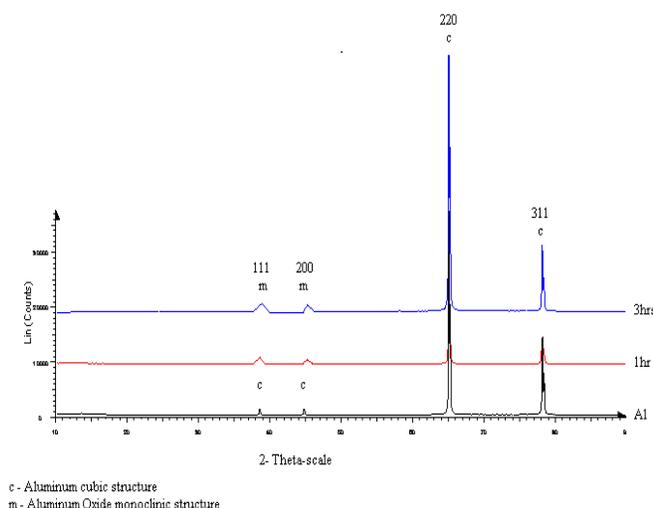


Figure.9 XRD patterns of anodized aluminum

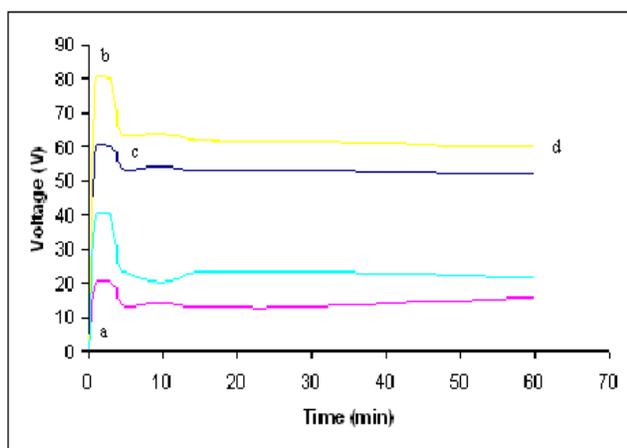


Figure.10 Voltage time graph of anodized aluminum at 20V-80V.

4. CONCLUSION

Porous alumina film was successfully fabricated at ambient temperature and at different voltages. The different voltages applied was found to produce pores that are not well ordered; the FE-SEM results shows the effect of voltage increment on the pore size, which clearly shows the relationship from ohms law between current, current density and voltage. Double the voltage doubles the current, increases the current density significantly and rate of chemical dissolution and pore formation proceed rapidly. The pore diameters were found to be dependent on the voltage and current density applied.

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