Influence of Anodizing Voltage on Formation of Porous Anodic Aluminium Oxide Thin Films in Mixed Solution of H_3PO_4 and CH_3COOH

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Abstract

A porous anodic aluminium oxide (AAO) thin film on aluminium was prepared in a mixed electrolyte of phosphoric acid and acetic acid solution. The growth and morphology of the film were investigated. During the anodizing process, the growth of AAO thin film is strictly influence by the anodizing parameter. The anodizing process was done by varying the anodizing voltage at 70 V to 130 V. The constant temperature of 10 °C to 15 °C was applied and the anodizing process was done in the solution of H_3PO_4 and CH_3COOH (H_3PO_4:CH_3COOH). The results indicate that the growth rate of AAO thin film increased with increasing the anodizing voltage. Morphology of the AAO thin film was examined by scanning electron microscope (SEM). Result shows that higher anodizing voltage led to the larger pore diameter. The pores also uniformly distributed on the substrate surface when the anodizing voltage reached to 130 V. From this study, the optimum parameters to obtain nanoporous AAO thin film with H_3PO_4 and CH_3COOH solution can be known. The anodizing voltage should be in the range of 70 – 130 V in order to produce pores below 100 nm in size.

Keywords: *Aluminium, Anodizing, Anodic Aluminum Oxide, Phosphoric Acid, Acetic Acid, Growth Kinetic, Pore Diameter.*

1. Introduction

Anodic aluminium oxide (AAO) thin films grown in acid electrolyte possess porous structure on substrate surface. The geometry of AAO thin film is characterized by a closely packed array of columnar hexagonal cells with nanopores at their centers [1]. AAO film has great applications. It is widely use in the manufacturing of hard disc, adhesives, templates for nanoparticles, quantum dots arrays, magnetic materials and also photocatalysts [2 - 8].

AAO thin films can be obtained by anodizing, which is a process for nanostructured material fabrication. The anodizing of aluminium has been widely studied because it always covered with a thin oxide film. This is the cause of aluminium has high affinity for oxygen which makes it an excellent corrosion resistant metal. [9, 10]. In anodizing process, there are several factors affected to the formation of AAO thin films which are anodizing temperature, voltage, electrolyte and also anodizing duration.

The nature of an electrolyte used for aluminium anodizing is a key factor which determines the type of oxides grown on the substrate surface [11]. AAO thin films were mainly grown in strongly acidic electrolytes such as sulfuric, oxalic, phosphoric and chromic acid solutions, where the resulting oxide film can be only sparingly soluble [11]. In this study, mixed acid solution was used to create AAO thin film with controlled morphology. Ma Song-Jiang et al. [12] has been reported that mixed acid solution as anodizing electrolytes can decrease the film dissolution rate, then increase the film formation efficiency and improve the film properties [12].

The mixture of phosphoric acid and acetic acid can create porous AAO thin film through oxidation and reduction reaction in anodizing process. The physical, chemical and electrical properties of this oxide film can be measured by anodizing process. However, the porous AAO thin film properties is strictly influenced by anodizing process parameter such as anodizing voltage, electrolyte temperature, acid concentration and duration of anodizing process. Thus, the study approach on anodizing process by using H_3PO_4 and CH_3COOH will be explored to obtain the nanostructured porous AAO thin film. The new hypothesis will be generated with explore the relationship between anodizing process parameter and formation of AAO thin film on aluminium substrate in order to enlarge its applications.

2. Experimental

The fabrication of aluminium substrate is 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 samples then were annealed at temperature 500 °C for two hours. The sample with 3 mm thick is grinded and polished by using diamond paste until mirror-like surface are obtained. The anodizing process was done by using mixed acid solution which is phosphoric acid (1.0 M) and acetic acid. Anodizing process was done at 70 V to 130 V at 10 °C to 15 °C for 60 minutes. The morphology and structure of porous AAO thin film obtained were characterized by Scanning electron microscope (SEM) model JEOL JSM-6460LA SEM.

3. Results and Discussion

3.1. Morphology of porous film

The effect of the anodizing voltage on film morphology was investigated. Figure 1 shows the morphology of the film anodized in four different voltages, 70 V to 130 V respectively. For anodizing with 70 V, the surface of oxide formed possessed irregular structure with small pores. The pores formed were non-uniform and discontinuity. Meanwhile, the pores formed in 90 V of anodizing voltage were more circular and separated by thick pore walls. The pores were possessed irregular structure and discontinuity. For 110 V, the pores were continuity formed on the surface and the pore structure become more open. The pores were also separated by the thick pore walls. By increasing the voltage into 130 V, the structure of pore was more circular with large opening. The pores also formed uniformly on the surface.

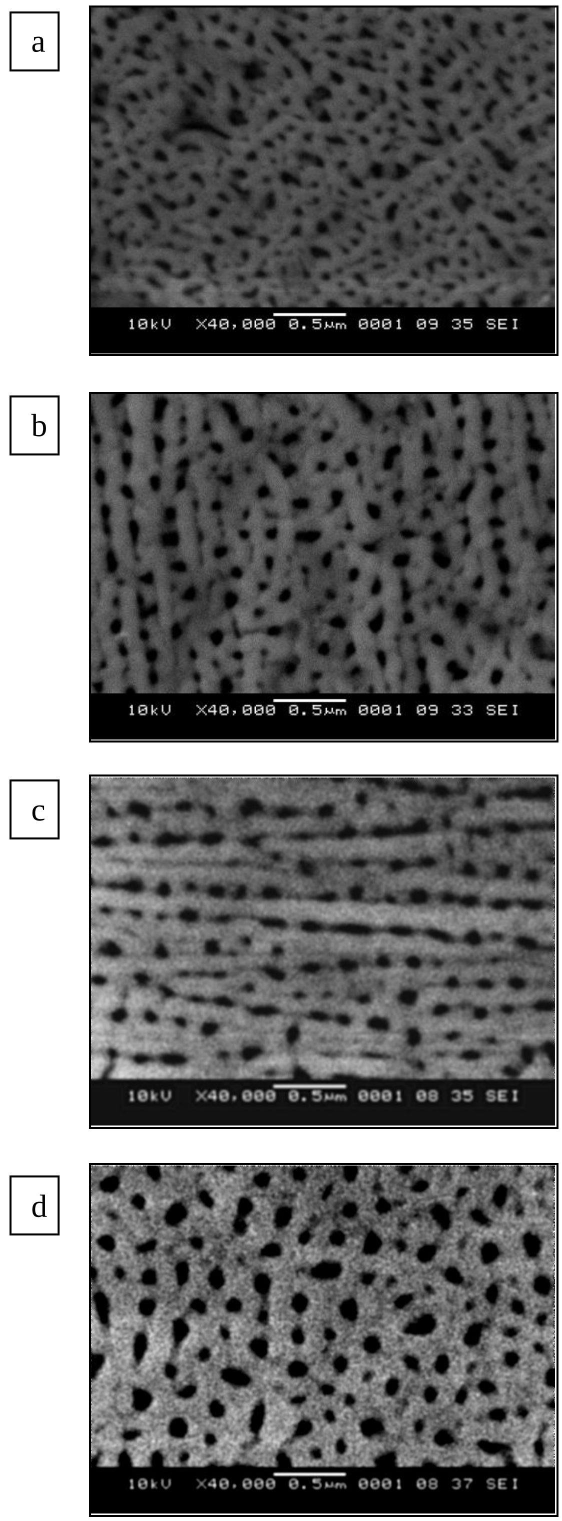

Figure 1: SEM images of AAO films formed in 1.0 M H_3PO_4 + CH_3COOH (a) at 70V, (b) at 90V, (c) at 110V and (d) at 130V.

3.2. Pore size

Figure 2 shows the average pore diameter for every sample anodized at 70 V to 130 V. Firstly, the graph was slightly decreased and then gradually increased the anodizing voltage increased. The average pore diameter anodized with 70 V was around 66 nm in size. The pores are more irregular and smaller. When increasing the voltage into 90 V, the average pore diameter becomes smaller which is around 61 nm. The substrate anodized with 110 V has larger pore diameter which is about 75 nm. When anodizing voltage up to 130 V, the average pore diameter becomes larger around 92 nm. The pores were uniformly distributed on the surface. This result is similar with Sachiko Ono et al. (2003), which have been reported that in anodizing with 0.4 M H_3PO_4, higher anodizing voltage resulted to larger pore size [13]. This is similar with Yan Zuo et al. (2006) which have been reported that the diameter of pores become larger as the anodizing voltage increased in the 0.6 M H_3PO_4 electrolyte [14].

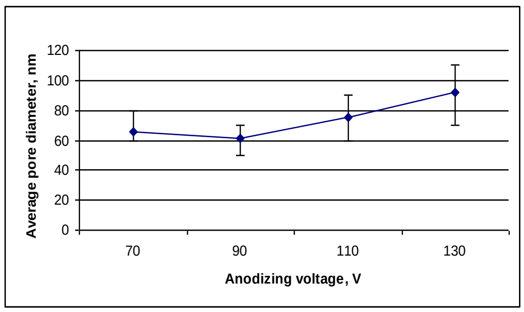

Figure 2: AAO pore diameter anodized with 70V to 130V.

3.3. Effect of anodizing voltage on formation of Porous AAO Thin Films

Figure 3 shows the effect of anodizing voltage on formation of AAO thin films on substrate surface. When the anodizing voltage increased, the percentage of substrate mass change also increased. For anodizing with 70 V, the mass of substrate decreased 0.16% after 60 minutes anodizing. When the voltage increased to 90 V, the total of mass change is 0.18%. For anodizing with 110 V, the percentage of mass change increased to 0.22%. For the higher voltage at 130 V, the percentage of mass change was around 0.25%. The increment of percentage of mass change in anodizing process shows that AAO thin film formed on substrate surface very well.

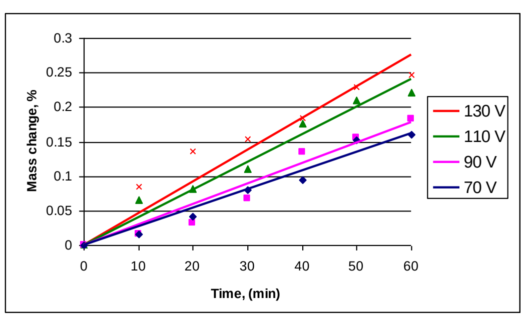

Figure 3: Effect on different voltage on formation of AAO thin film.

4. **Conclusion**

During anodizing of aluminium in 1.0 M H_3PO_4 + CH_3COOH, porous AAO thin films are formed. Result for surface morphology and kinetic reactions of the films by varying the anodizing voltage were obtained. Higher anodizing voltage at 130 V led to the larger pores diameter which is around 92 nm and the pores were uniformly distributed on the substrate surface. The percentage of weight change increase by increasing the anodizing voltage. It shows that AAO thin films growth successfully on substrate surface at high anodizing voltage and resulted to the large pore size. This study showed that H_3PO_4 + CH_3COOH are suitable electrolyte for growing porous film on aluminium surface with controlled morphology. 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 70 – 130 V in order to produce pores below 100 nm in size.

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