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A Novel Process to Produce Nano Porous Aluminum Oxide Using Alkaline Sodium Phosphate Electrolyte

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Abstract: In this study, we report the fabrication of nano porous aluminum oxide film for the first time, in alkaline sodium phosphate electrolyte at ambient temperature using a single step anodization approach. A novel method has been developed to prepare the electrolyte, by simply titrating the phosphoric acid with a base for preparation of new types of Anodized Aluminum Oxide (AAO) at pH 13. The anodization process was controlled by a dc voltage of 20 V applied across the electrochemical cell. Using this method, we have been able to obtain nano porous aluminum oxide with pore diameters between 50-100 nm. Apart from the influence of the current density, traces of sodium and phosphorus present in the porous alumina also makes a significant contribution to the formation of nano pores.

Key words: Anodization, electrolyte, microstructure, nano porous materials, X-ray diffraction

INTRODUCTION

In the past decade, there has been a particular focus on the fabrication of porous aluminum oxide film, because of its unique physical and chemical properties (Heilmann *et al.*, 1999). Generally, it is well known that a carefully controlled anodization of aluminum in an acidic electrolyte produces a thin film of dense aluminum oxide underlying an ordered array of smaller sized nanopores (Belwalkar *et al.*, 2008). In basic media, a barrier-type, corrosion-resistant, oxide film is produced (Christof *et al.*, 2001). The nano pores produced from acid electrolytes, are used in magnetic storage devices, catalytic membranes and photonic crystals etc. (Singh *et al.*, 2005). The film from the alkaline electrolytes, are used as dielectric (for electrolytic capacitors) or insulating films (Christof *et al.*, 2001).

Many researchers have reported fabrication of nano porous aluminum oxide from oxalic acid (Hou *et al.*, 2002; Li and Huang, 2007; Su *et al.*, 2008), sulfuric acid (Belwalkar *et al.*, 2008; Sulka *et al.*, 2002; De Azevedo *et al.*, 2004; Sulka and Parkola, 2007; Kang *et al.*, 2007) phosphoric acid (Chu *et al.*, 2003; Wang *et al.*, 2008) and mixed acids (Sachiko *et al.*, 2005; Yufei *et al.*, 2006). The use of alkaline electrolyte has been reported (Vergara *et al.*, 2007). Vergara *et al.* (2007) used 0.13 M borax electrolyte at 60 V to produce 240 nm porous anodic alumina at a temperature of 333 K with pH 9. The cross sectional view of the TEM results displayed makes it very difficult to confirm the nano pores formed.

In this study, we report a simple method to prepare alkaline electrolyte to fabricate nano porous aluminum oxide at ambient temperature, for the first time to the best of our knowledge.

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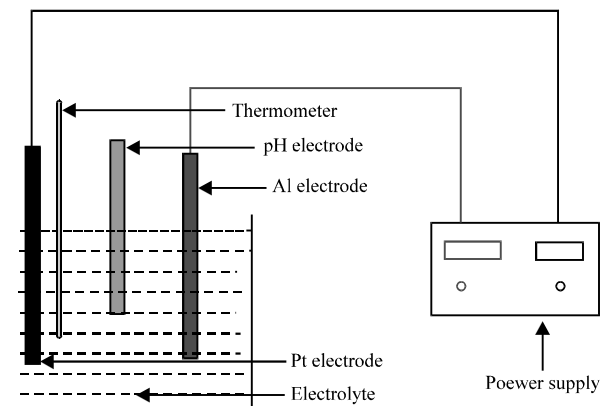


Fig. 1: Electrochemical cell used for anodization of aluminum

A schematic representation of the setup is shown in Fig. 1. We examine the effect of the alkaline electrolyte on the nano porous aluminum oxide formed.

MATERIALS AND METHODS

The high purity aluminum foil (Al 99.3%, thickness 0.3 mm) is purged by acetone in ultrasonic cleaner to clean out possible grease on its surface (Zhu *et al.*, 2005). Then, the sample is electropolished in 1:4 volume mixtures of HClO_4 and $\text{C}_2\text{H}_5\text{OH}$ at constant current density of 500 mA cm^{-2} for 1 min at 10°C (Grzegorz and Wojciech, 2009). The alkaline electrolyte was prepared by titrating 20% phosphoric acid with 2.5 M sodium hydroxide until it attains a pH of 13. The electrochemical bath for the anodization process consists of platinum electrode as the cathode electrode and aluminum foil as the anode electrode. The prepared aluminum foil, after having been rinsed with de-ionized water was anodized for 2 h under a dc voltage of 20 V in sodium phosphate electrolyte at ambient temperature.

Characterization of the nano pores were performed by scanning electron microscope (Model Supra 35VP), X-ray energy dispersive spectroscopy (EDX), X-ray diffraction patterns (Bruker D8 Advance X-ray diffractometer with Cu target) and current density-time response graph.

RESULTS AND DISCUSSION

Figure 2 shows SEM micrograph of the surface view of porous aluminum oxide after anodization at 20 V in sodium phosphate electrolyte at ambient temperature. The diameters of the pores is $\sim 70 \text{ nm}$ and the inter pore distance is $\sim 100 \text{ nm}$. Moreover, the morphology of the surface shows that the pores are uniformly distributed but with irregular shapes. In the initial stage of anodic oxidation of the film, discontinuous O_2 bubbles can be seen at the surface of the anode. The transfer of Al^{3+} and O^{2-} across the barrier alumina under constant electric intensity and Al_2O_3 was generated as a result.



Along with anodic oxidation, barrier oxide film was formed on the surface of the metal, when the voltage increases O^{2-} in alumina was oxidized (Zhu *et al.*, 2005).

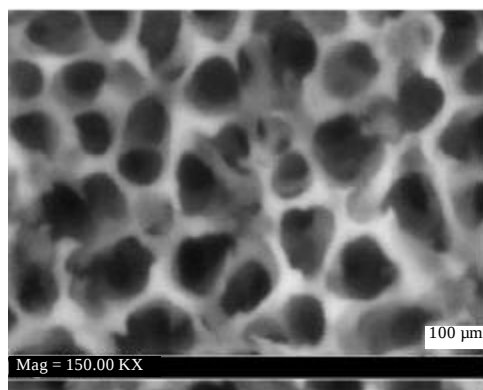


Fig. 2: Scanning electron micrograph of the top view of aluminum after anodizing for 2 h at 20 V in sodium phosphate electrolyte at ambient temperature

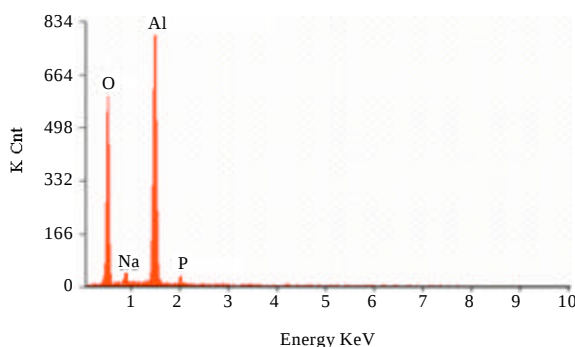
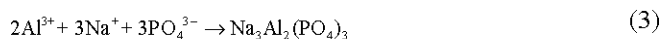


Fig. 3: EDX of aluminum anodized at 20 V in sodium phosphate electrolyte at ambient temperature



and Al^{3+} injects into the electrolyte at the vicinity of solution/films interface.



The second reaction proceeds first at these places in which nano pores are developed by the dissolution of alumina. The nano pores make the current density higher than around the local regions. This nano porous structure that are gradually formed enable one to make thin cylinders with controlled diameters as small as a few nm and this can be used as host for growth of nanowire, nanotube and nano devices through template synthesis. The diameters of the nano pores are comparable to those produced in the acid medium, previously alkaline electrolyte is not known to produce porous alumina structure but barrier type oxide film, the presence of Na^+ and PO_4^{3-} in addition to the current density makes it possible.

The Energy-Dispersive X-ray spectroscopy (EDX) analysis of the nano porous aluminum oxide is shown in Fig. 3. The EDX spectrum indicates that the nano porous

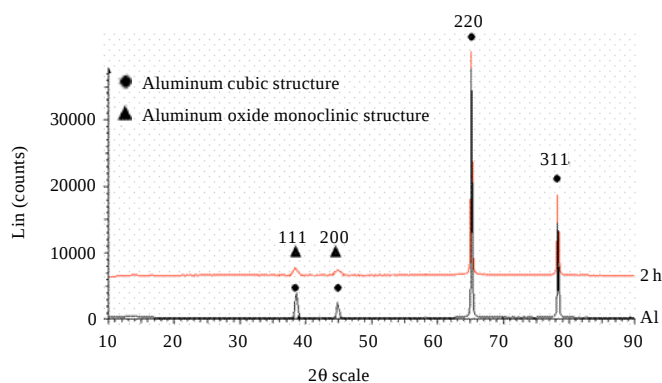


Fig. 4: XRD patterns of aluminum after anodizing for 2 h at 20 V in sodium phosphate electrolyte at ambient temperature

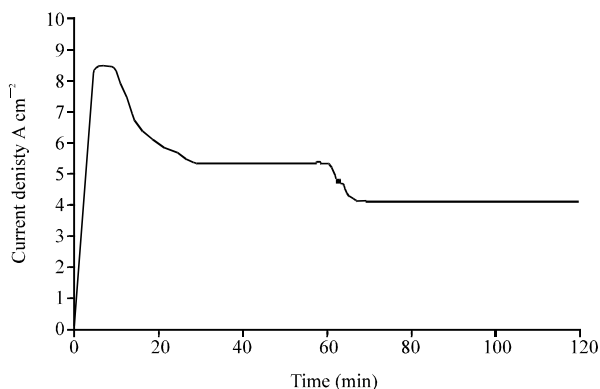


Fig. 5: Current density-time response for aluminum anodized for 120 min at 20 V in sodium phosphate electrolyte at ambient temperature

aluminum oxide is composed of Al, O, Na and P. The analysis indicates that the ratio of Al and O in the pores calculated from the EDX data are in agreement with corresponding value of bulk alumina. The minute amount of Na and P present as a result of the bond energy and difficulty in being adsorbed at the surface of the film confirms the prepared electrolyte to be sodium phosphate.

X-ray diffraction measurement is carried out to investigate the phase transformation of the porous aluminum oxide in Fig 4. The observed FCC to monoclinic diffraction peaks is assigned to 39° and 45° on the 2θ scale, corresponding to diffractions from (111) and (200) planes. The other diffraction peaks can be assigned to the aluminum substrate.

The porous anodic alumina film developed in this sodium phosphate electrolyte is as a result of oxide film dissolution, stress concentration, high pH and the changing of current density are the main causes of porous film development (Zhu *et al.*, 2005). Therefore, the current density-time behavior of aluminum anodized in sodium phosphate electrolyte at 20 V for 2 h at ambient temperature is shown in Fig. 5 which resulted in (1) a surge to high currents, reaching a maximum of 250 mA caused by pore nucleation, (2) drop in current after 10 min indicates slow dissolution process, (3) partial current density stability after 25 min

indicates pore growth and (4) a main period of steady current density after 70 min. This steady current density appears when the rate of aluminum oxide dissolution occurring at the base of pores equals the rate of oxide formation at the metal-oxide interface. From that moment a stable growth of the porous oxide layer on anodized aluminum starts.

CONCLUSION

In conclusion, we have successfully prepared nano porous aluminum oxide film using a titration technique to prepare the electrolyte. The growth of the nano pores in the alkaline electrochemical cell was ascribed to the current density and pH. The results of the XRD and EDX suggest that the composition of the fabricated nano pores is alumina with traces of sodium and phosphorus. The fabricated nano pores are promising platforms for various electronic and magnetic devices.

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