



The nanoporous anodic alumina oxide formed by two-step anodization

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ABSTRACT

The nanoporous anodic aluminum oxide (AAO) was fabricated by two-step anodization technique. The effects of anodization electrolyte and time on the pore diameter and structural properties of the AAO were investigated. The Field Emission-Scanning Electron Microscopy was used for the analysis of the surface morphology of AAO structure. The nanoporous structures with the pore size in the range of 31–113 nm and oxide layer thickness 3.4–33 μm were obtained. Wetting properties of these surfaces were characterized by measurements of the water contact angle. It was seen that the surface of the AAO became hydrophilic with the increase in the anodization time. Furthermore, we explored the mechanical properties and thermal stabilities of the AAO by microhardness and thermo-gravimetric analysis measurements. It was found that the AAO structures synthesized in the electrolyte containing ethylene glycol solution have the highest hardness and display well thermal stability among the other structures. The surface area and crystal structure of AAO were determined by surface area analysis and X-ray diffraction patterns measurements. Experimental results showed that the AAO structures have amorphous phase and the highest surface area is 2.59 m²/g.

1. Introduction

Nanostructures such as nanopores, nanotube, nanorods, and nanowires provide various advantages in advanced application areas, due to their unique physical, chemical, mechanical, and optical properties [1–6]. Anodic aluminum oxide have attracted much interest due to a regular arrangement of nanopore structures, ease to control the nanopore diameter, high surface area, low cost, excellent thermal stability, being non-toxic and biocompatibility [7]. Due to this, the AAO structures have extensively found use in application areas such as filtration process [8], biosensor [9], drug delivery [10], corrosion resistant [11], oxygen sensor [12], catalysis [13], photocatalytic [14], cancer therapy [15], DNA sensor [16], electrochemical biosensor, [17], separation [18], and fluorescence detection [12]. Moreover, the geometrical arrangement of the nanopore makes it possible to use alumina as a template for synthesis of various nanostructures [19,20]. Especially, studies on semiconductors and dielectrics have introduced AAO as a very promising template material for the deposition of nanostructures. In the literature [21], in order to prepare flat and homogeneous chitosan/phosphotungstic acid polyelectrolyte membrane of controlled thickness for use in low temperature H₂/O₂ fuel cells, the nanopore alumina membranes have been used as support materials. In this framework, anodic alumina membrane was filled with cesium ammonium sulphate tellurate as proton conductor and performance of this

electrolyte supported by anodic alumina membrane was investigated in H₂/O₂ fuel cell working [22]. AAO, which can be easily integrated with micro fuel cell, is highly preferred in terms of low cost. It has recently been shown that this anodic alumina membrane template can be extended to the preparation of one dimension metal oxide and hydroxide nanowires and nanotube [19]. Bocchetta et al. [19] reported that anodic alumina membrane as a template was used to produce cerium-cobalt mixed oxide nanotubes in an adjustable composition at room temperature by electrochemical method. Bocchetta et al. [20] synthesized Cd(OH)₂ nanowires deposited into pores of anodic alumina membrane template via cathodic electro-synthesis from the aqueous solution containing Cd(NO₃)₂ at room temperature.

In many applications, the control of nanostructure shape and geometry is critical. Porous anodic alumina can be easily obtained by controlled anodization of aluminum surfaces in aqueous acids [23–25]. To obtain the self-ordered AAO, two-step anodization method has been proposed by Masuda and other workers [26–28]. The first-step anodization under convenient conditions causes the formation of an irregular oxide layer [24,29]. Nevertheless, the formation of irregular oxide can lead to generation of regularly deployed nanoconcaves on an aluminum surface. Afterward, the irregular oxide layer is chemically removed and the obtained nanoconcave structure serves as nucleation sites for the pore initiation for yielding highly ordered arrays in second-step anodization [25, 30]. Zaraska et al. [29] reported that the self-organized

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two-step anodization process allows obtaining best hexagonal pore arrangement. As described in the literature [2, 4, 5, 24, 29], the most important controllable parameters affecting the creation of nanoporous alumina are the anodizing voltage or current density, anodization time, type/concentration of the electrolyte, pH, and temperature. Under conventional anodization conditions, three different electrolytes including sulfuric, oxalic and phosphoric acids are commonly used for anodization processes [24,31,32]. Norek et al. [33] have investigated the effect of ethylene glycol addition to an oxalic acid electrolyte on the morphology of anodic aluminum oxide. It was determined that the AAO structure having different pore diameter occurs in the presence of ethylene glycol owing to a broad incorporation of soluble $C_2O_4^{2-}$ and COO^- ions [33]. Otherwise, It was noticed in the literature that porosity of nanostructures reduces with increasing of anodization potential in sulfuric acid [34,35] and oxalic acid electrolytes [36].

The main aim of the present work is to influence of different anodization conditions such as the electrolyte type and anodization time on the morphology of AAO formed by two-step anodization method. The structural and morphology of the AAO structures obtained in the electrolytes containing oxalic acid and ethylene glycol were investigated using the Field Emission-Scanning Electron Microscopy (FE-SEM) and X-ray diffraction (XRD). Moreover, the effects of the variation of anodization time on the resulting surface morphology of the AAO structures were examined. The wetting behavior of AAO structures having different pore size distribution was determined by analyzing the contact angle. Furthermore, the thermal stabilities, microhardness properties and surface areas of the AAO structures were researched.

2. Materials and methods

2.1. Materials

Oxalic acid ($C_2H_2O_4$), ethylene glycol (99.5%), phosphoric acid (H_3PO_4 , 88%), perchloric acid ($HClO_4$, 60%), chromic acid (H_2CrO_4), acetone and ethanol were purchased from Merck company. The working electrode was aluminum alloy 1050 sheet with the following chemical composition (wt%): 0.40, Fe; 0.25, Si; 0.05, Cu; 0.05, Mn; 0.05, Zn; 0.03, Ti; 0.05, V; 0.03, the rest is Al. All the chemical reagents were analytical grade without further purification. All experiments were carried out at room temperature using distilled water.

2.2. Preparation of AAO electrodes

The aluminum sheet with 0.4 mm thickness was cut into coupons (1 cm × 1 cm) and then was degreased in acetone, washed with de-ionized water. Al electrode was annealed in an air furnace at 500 °C for 5 h. Prior to anodizing, Al sample was electrochemically polished in a mixture of perchloric acid (60 wt%) and ethanol (1:4 vol.) under the constant voltage of 20 V for 1 min at 5 °C. After electropolishing, the sample was rinsed with water and ethanol and then dried. Anodization experiments for the fabrication of AAO were carried out using DC power supply with a conventional two-electrode system in potentiostatic mode at a constant voltage of 50 V. Aluminum sheet was used as the anodic electrode while platinum (10 × 10 × 0.1 mm) was used as the cathodic electrode. To create regular nanopores arrays without the presence of surface debris on the Al surface, two-step anodization process was performed. As can be seen Fig. 1, in the first-step anodization, the Al sheet was anodized at 50 V for 1 h in 0.3 M oxalic acid ($H_2C_2O_4$) electrolyte. After the first-step anodization, as obtained irregular oxide layer was removed by chemical etching in a mixture of 0.4 M H_3PO_4 and 0.2 M H_2CrO_4 at 100 °C for 1 h. Then, the second anodization was carried out on the same Al sheet in two different anodization baths. AAO electrodes were formed at anodization potential of 50 V for the anodization times of 1, 2, 4 h in 0.3 M $H_2C_2O_4$ electrolyte (coded as A electrolyte) at 20 °C and at anodization potential of 50 V in the mixture of 1:1 water: ethylene glycol electrolyte (V:V) containing

0.3 M $H_2C_2O_4$ (coded as B electrolyte) for the anodization times of 2, 4, 8 h at 20 °C. Finally, to widen the pores of the AAO electrode, samples were immersed in 0.5 M H_3PO_4 solution at the temperature of 20 °C. Then, samples were immediately washed in distilled water and consequently dried in air. The AAO electrodes were annealed at 550 °C for 2 h in the atmosphere.

2.3. Characterization of AAO

The surface morphologies of electrodes were examined by FE-SEM. The FE-SEM images were taken using a Zeiss /Supra 55 SE instrument at high vacuum and 10.00 kV EHT. The structural analysis of the AAO was performed by XRD (Rigaku Smart Lab diffractometer), by using $Cu-K\alpha$ radiation and operated at 40 kV and 30 mA with a scan rate of 3° min^{-1} . The contact angle measurements were performed handling the sessile droplet method with 5 μL droplets of deionized water as the solvents by using a KSV Attension Theta Lite TL 101 Optical Tensiometer. Thermal analyses of AAO electrodes were carried out by Shimadzu DTG-60H simulated thermogravimetry/differential thermal analysis (TG/DTA) with the heating rate of 10 °C/min under N_2 atmosphere. The mass was recorded as a function of temperature. The average pore size, pore volume, and surface area were determined by nitrogen adsorption/desorption porosimetry (Micromeritics Gemini VII Surface Area and Porosity). Shimadzu HMV-G microhardness tester with a load of 4.903 N and a dwell time of 7 s was utilized to measure the Vickers hardness.

3. Results and discussion

3.1. Synthesis and characterization of AAO

Fig. 2 displays changes in the current density with the time recorded during second anodization in A and B electrolyte at 50 V, respectively. It is seen that the current density increases up to 6 min and then it gradually decreases roughly in both anodizing electrolytes. At the first stage of anodization, thick alumina layer with a dense and highly disordered porous structure showing a broad pore size distribution is formed. An exponential increase of the current density is observed until a maximum is reached, after which the current decreases. During this step, a rearrangement of the pores occurs in order to grow nanoporous. After this stage, the decrease of the anodization current density with time has been associated to the rapid increase of the nanopores length, which lengthens the diffusion path of the ionic species [37–40]. The current density starts to decrease earlier as a consequence of Ethylene glycol addition. This can be explained by the lower solubility of Al_2O_3 in an Ethylene glycol-water mixture with respect to the aqueous solution. Moreover, it is also possible that the higher ohmic drop in the ethylene glycol containing electrolyte, reduces the potential drop across the growing layer with consequent reduction of the anodic current.

Structural features and degree of the hexagonal arrangement of AAO created on different anodizing electrolytes and times were studied on the basis of FE-SEM images. Fig. 3 shows FE-SEM images and the contact angles of the Al sheet, AAO obtained by the first-step anodization technique and Al sheet obtained by removing the oxide layer after the first-step anodization. As shown in Fig. 3(a), the natural oxide layer existing in the Al layer was cleaned by electropolishing and rough strip patterns were observed on the surface. The FE-SEM image of the AAO formed by the first-step anodization process in A electrolyte was seen in Fig. 3(b). The result shows that the irregular oxide nanopores formed on polished Al sheet. From the images (Fig. 3(b)), pore diameter was found to be about 34 nm. Similar results for AAO arrays formed by first-step anodization technique were reported by Kim Hoon et al. [41] and Fang et al. [42]. Fig. 3(c) presents the obtained structure after removal of the oxide layer grown during the first-step of anodization. As can be seen, the hexagonal structure has occurred on the surface and the diameter of hexagonal arrangement was determined to be

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