THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 2 – 2013, ISSN 1453 – 083X

PREPARATION AND CHARACTERISATION OF ALUMINA TEMPLATE OBTAINED BY ONE-STEP ANODIZATION METHOD

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ABSTRACT

The goal of this study was to obtain an alumina template (AAO) by one-step anodization method and to evaluate its optical properties correlated with the annealing temperature. AAO was obtained from two different media: sulphuric acid (1.5 M H_2SO_4) and oxalic acid (0.4 M $H_2C_2O_4$) at a potential of 15 V and 40 V, respectively. AAO morphology and chemical composition had been investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The average pore diameters such as 20 nm for AAO obtained from H_2SO_4 and 40 nm from $H_2C_2O_4$ were measured. The crystalline structures of AAO samples annealed at three different temperatures of 150ºC, 300ºC and 350ºC were studied by X-ray diffractometry (XRD). The effect of annealing temperature on the optical properties of AAO was studied by UV-VIS spectrophotometry.

KEYWORDS: anodization, alumina template, SEM, EDX, XRD, optical properties

1. Introduction

Nowadays the porous alumina is used as the most common template material for fabricating of inorganic templates and also nanowires due to the alumina template (AAO) advantages. These are the adjustable pore diameters, uniform tubes, highly ordered porous structure [1], a reliable fabricating process with a low cost, and good thermal and chemical stability. An advantageous production method for AAO is the anodising process of aluminium from acidic electrolyte solutions with a cylindrical cell structure [2, 3] and hexagonal pattern [4]. AAO ceramic oxide has a large number of applications in high-temperature range without deformation, whereas a commercial material (Whatman Anodiscs®) cracks could appear above 700ºC due to the high mechanical tension arising from a phosphorous gradient along the pore direction [5].

Also, alumina (Al_2O_3) has lots of applications as an optical material, i.e. in thin-film devices. In this field the electronic structure and bonding presented in Al_2O_3 are intensely studied. Practically, the optical properties have a high interest calculating the optical constants of Al_2O_3 [6, 7] with high accuracy. These properties can be analysed using atomic force microscopy (AFM) [8], and reflectance spectroscopy techniques at room temperature [9] and high temperature [10].

The goal of this study was to obtain the AAO by one-step anodization method from two different media and to characterize the AAO morphology and structure by means of scanning electron microscopy (SEM) technique. Then, as-prepared AAO is crystalline to X-ray diffraction (XRD). XRD and thermal treatment techniques have been used to characterize the crystalline phase transitions of AAO prepared in oxalic acid [11] and sulphuric acid [12] at temperatures up to 150ºC, 300ºC and 350ºC respectively. For the synthesis of AAO regular pore matrix, a pre-treatment by polishing, chemical degreasing, etching and pre-texturing was required [13]. Also, the correlation between the AAO optical properties and annealing temperatures was evaluated.

2. Experimental details

High purity aluminium foil (95% Al, 50mm by 50mm and 2mm thick) was used as a substrate material for template. Aluminium with a high purity

is usually recommended to obtain self-ordered porous alumina. The quality of substrate surface has major influences on the nanostructure by self-organized anodization. Firstly, these pieces were mechanically polished with SiC paper with different granulations, and then cleaned and activated following the next steps. These procedures consist of an organic degreasing in acetone for 10 min, chemical degreasing in 1M NaOH for 5 min, etching by immersion in 5% HNO_3 for 5 min, rinsing with distilled water, and then drying in air.

Two AAO development stages are summarised into the below schematic diagram. Fig. 1a shows the aluminium surface pre-treated like substrate for the following alumina layer, before the anodization. Fig. 1b indicates the aluminium anodised with channels growing nano-sized [14].

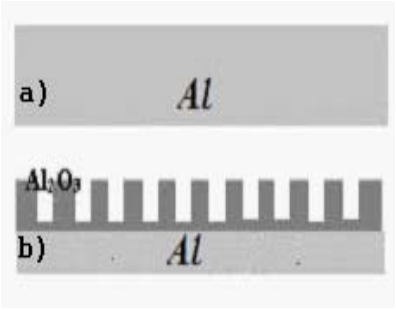


Fig. 1. *Schematic diagram of AAO development on aluminium layer a) before and b) after the anodic process*

A standard two electrod system with a cell (Fig. 2) volume of 500 mL connected at a PM 2813 programmable power supply were used to perform the anodization process. Both cathode and anode were aluminium plate electrodes. This study approached the AAO synthesis by one-step anodization method. During the anodic process both aluminium faces with a circular sector shaped are exposed to acidic solutions. Each AAO was fabricated in 0.4M oxalic acid ($H_2C_2O_4$) electrolyte and 1.5M sulphuric acid (H_2SO_4) at lower than room temperature (18°C). The alumina layer has grown by passing a direct current (DC) through solution. The anodization voltage scheme consists of 60min exposure time at 15V and 40V respectively.

The passing current through aqueous solution produces hydrogen reaction at the cathode surface and oxygen with alumina at the anode surface (1). Aluminium anodizing performed in acidic solution slowly dissolves the alumina layer obtained. The aluminium oxide dissolution process is balanced with the oxidation ratio to nanopores [15, 16].

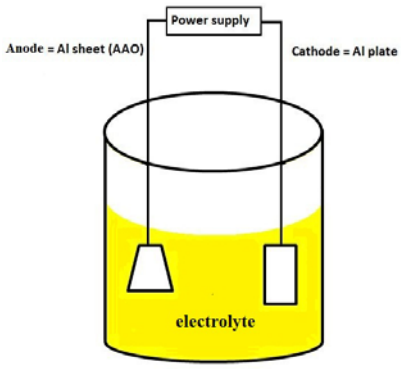


Fig. 2. *Experimental set-up of anodization cell*

$$Al(s) \rightarrow Al^{3+}(oxide) + 3e^{-}$$
$$\frac{3}{2}H_2O(l) \rightarrow 3H^{+}(aq.) + \frac{3}{2}O^{2-}(oxide) \quad (1)$$

Aluminium substrate and AAO morphological characteristics were analysed by means of SEM technique using EVO 50 EP microscope (Karl Zeiss SMT AG, Germany). The micrographs were picked-up at (2÷5) kV using the secondary electron detector. For better conductivity during SEM examination, samples were prepared by means of sputering technique with an ultra-thin platinum layer.

Three AAO samples obtained from oxalic solution were heat treated (annealed) to different temperatures (150ºC, 300ºC and 350ºC) consisting of introducting them in furnace L312 P320 Nabertherm for 3h.

The crystallographic characteristics of the annealed samples were analysed by means of XRD using DRON-3M diffractometer. XRD spectra were recorded at room temperature, and diffractometer using CoK_α radiation (λ = 1.79Å) in 2θ configuration ranged between 40º and 70º, at 40kV tension and 30mA current intensity with a scanning speed of 0.02º min^{-1} and acquisition time of 1 s/step.

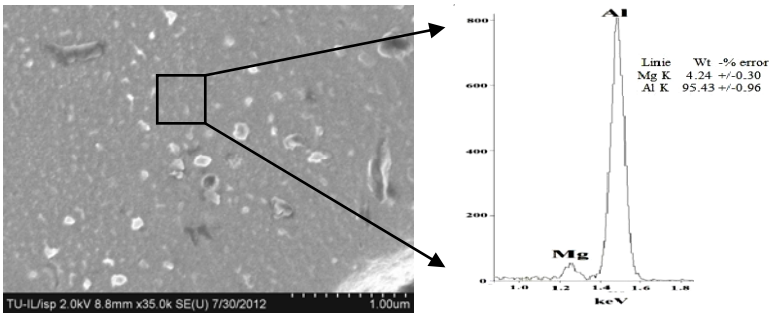
Also, for all samples the reflectance measurements were recorded by means of spectroscopy method using Perkin Elmer 35UV-VIS spectrophotometer with a spectral range of (190÷1100) nm.

3. Results and discussion

SEM plan view of the aluminium foil morphology after the required pre-treatment and before the anodic process is shown in Fig. 3a. The aluminium surface is still slightly rough and for future experiments an electropolishing treatment is again required.

It is well-known that anodization of aluminium containing impurities could lead to defects.

Aluminium chemical composition of a homogeneous selected area (Fig. 3b) was determined by means of energy dispersive X-ray spectroscopy (EDX).



a) *b)*

Fig. 3. *Aluminium substrate: a) morphology (35.000×) and b) chemical composition*

Aluminium substrate used in these experiments contain 95 wt.% of Al and 5 wt.% of Mg.

Fig. 4 reveals a plan view of the as-prepared anodic films (before thermal treatment) obtained from sulphuric acid at 15V (Fig. 4a) and oxalic acid at 40V potential (Fig. 4b).

Their morphology showed an ordered porosity, similar to Keller's model [17].

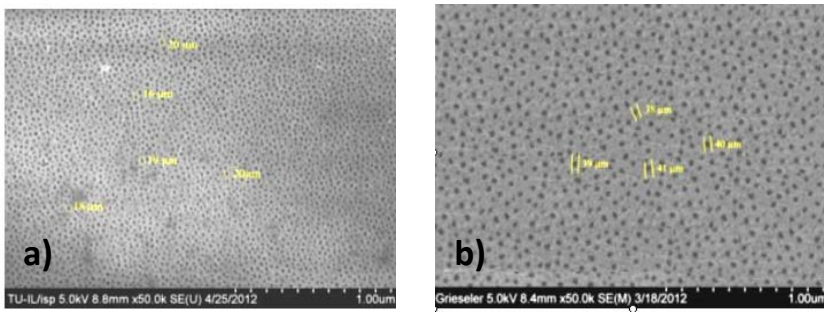


Fig. 4. *SEM images (50.000×) of porous oxidized templates produced by one-step anodization in: a) sulphuric acid and b) oxalic acid*

The average pore diameters were measured and revealed 20nm for the pores obtained from sulphuric acid and 40nm for those obtained from oxalic acid showing a hexagonal lattice.

Consequently, it was observed a change of the physical and chemical properties as well as of the anodic oxide film colour (different grey intensity). Pores diameter and interpores distance varied with anodization parameters such as type and concentration of the electrolyte, temperature, impurities and applied potential during the anodic process. The results are in concordance with the literature [18].

The internal structure of the AAO annealed samples was analyzed at room temperature by means of XRD method. A crystallization process varied with the annealing temperature showing α- and θ-(Al_2O_3) phases.

Diffraction patterns of AAO annealed at 150ºC, 300ºC and 350ºC are shown in Fig. 5.

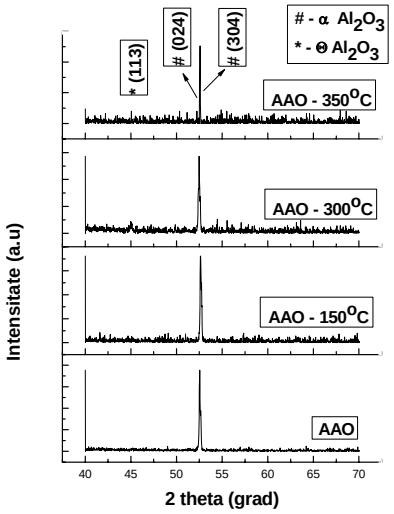


Fig. 5. *XRD patterns of AAO (obtained from $H_2C_2O_4$) annealed at 150ºC, 300ºC and 350ºC*

AAO is annealed below the melting point of aluminium, that is 680ºC, to obtain a large grain size.

XRD result of annealed AAO shows (113) plane at 2θ = 45º, (024) and (304) planes appeared at 2θ = 51.5º and 52.5º, respectively AAO structure became more crystalline with the annealing process relieving θ- and α-(Al_2O_3) phase. The annealing temperature changes the crystal structure of the alumina (θ hexagonal and α rhomboedric). The values of the diffraction peaks are in accordance with both standard JCPDS alumina card (MP 1323 and MP 1423).

Reflectance curves of annealed AAO at different temperatures are indicated in Fig. 6. Linear shape of curves is shown in the UV region where the reflectance coefficient values are constant (R~0.005%). VIS interested region presents the reflectance plots easily distinguished. AAO adsorbent and reflective features with increasing the annealing temperature are highlighted.

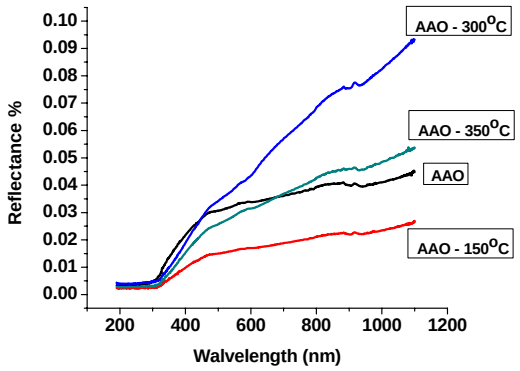


Fig. 6. *Reflectance spectra of AAO (obtained from $H_2C_2O_4$) annealed at 150ºC, 300ºC and 350ºC*

AAO annealed sample at the lowest temperature of 150°C has been oxidized having darker and more opaque visual aspect. Thereby, AAO high adsorption level was marked out because the oxide compounds forming on the template surface were compared with other two samples [19]. Increasing annealing temperature can determine pores agglomeration [20, 21].

This fact is confirmed by the pores widening and the interpores distance reducing differentially. Therefore, template surfaces became slightly rough favouring their reflexion ability. At 300°C and 350°C, respectively, the reflectance coefficient has increased and also the spectral curves show increased amplitude. Increasing wavelength the reflectance plots suddenly follow an exponential increasing as function of annealing temperature variation in IR region.

4. Conclusions

The alumina template was obtained by one-step anodization method from oxalic and sulphuric acid electrolytes at different parameters. A pre-treatment of aluminium substrate is required to assure the quality surface to obtain self-ordered porous alumina. The roughness degree of substrate was the most important factor which can influence the nanopores linearity and symmetry respectively. The template morphologies show a hexagonal lattice of nanopores with an average diameter of 40nm for them obtained from oxalic acid and 20nm from sulphuric acid. A changing of AAO physical and chemical properties as well as of the anodic oxide film colour (different grey intensity) due to the anodization parameters such as type and concentration of the electrolyte, temperature, impurities and applied potential during the anodic process was observed. The internal structure of AAO annealed samples was analyzed at room temperature by means of XRD method. The crystallization process varied with the annealing temperature showing α and θ-(Al_2O_3) phases.

The alumina reflectance as function of radiation wavelength for AAO annealed at different temperatures was observed. AAO absorbent and reflective features with increasing the annealing temperature are highlighted. The high absorbance ability is proved by AAO produced in $H_2C_2O_4$ and annealed at lowest temperature of 150°C in VIS spectrum.

Finally, this model was the basis for initial studies that aimed at better understanding of the physical and chemical properties of porous alumina and obtaining promised cobalt nanowires in self ordered alumina.

Acknowledgement

This work was financially supported by the Project SOP HRD - TOP ACADEMIC 76822. The authors gratefully acknowledge Dr. Adriana Ispas for guidance and SEM measurements. We are grateful to Andreas Bund and Udo Schmidt from Technische Universität Ilmenau, FG Elektrochemie und Galvanotechnik, Ilmenau, Germany for the efficacious discussions and advices. The authors would also thank Prof. Dr. Viorica Musat for the annealing treatment.

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