

POROUS ANODIC ALUMINA FILMS OBTAINED BY TWO STEP ANODIZATION

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Abstract: *The paper presents a preliminary study on the obtaining of nanoporous alumina membranes by two step anodization. Using this process, self-ordered porous structures can be obtained with variable distance between pores, high pore density on surface compared to membranes obtained by other methods. After the first anodization, the formed aluminum oxide was removed by chemical etching in a mixture of phosphoric acid and chromium trioxide. The second anodization, intended to obtain the self-ordered porous structure, was done at the same conditions as the first one. These membranes can be used for micro fluidic separation, sensor elements, as ideal templates for the formation of various nanostructured materials.*

Key words: *porous alumina, anodization, nanostructures, nanopores, self-organization.*

1. Introduction

Anodization is an electrochemical process that leads to the formation of a thick compact oxidic layer on the surface of a metal substrate. This type of non-porous surface layer normally increases the corrosion and wear resistance of metals. This method has been applied to several metals: aluminum, magnesium, niobium, tantalum, titanium, tungsten, vanadium, zinc, zirconium etc. Alumina films are the most commonly used in order to protect the surface of aluminum alloys. The two step anodization process for obtaining self-ordered alumina nanostructures was mentioned for the first time in 1995. This increasing attraction for these types of membranes is mainly due to their easy and relatively low cost processing [1].

In a typical anodizing process, an aluminum plate is connected to the anode of a DC source. A weak acid solution is used as electrolyte. The cathode can be made from any conductive material that is chemically inert in the electrolyte used. When applying tension, hydrogen ions are reduced in order to form hydrogen gas at the cathode and aluminum is oxidized into Al^{3+} cations. Some of these cations are dissolved in the electrolyte, and a part forms an oxidic layer on the metal surface. For further reaction, oxygen containing anions are supplied by the electrolyte.

Depending on the electrolyte used, two types of anodized alumina oxide layers can be obtained: thick barrier compact layers and porous oxide films. The adherent, non-porous and non-conducting barrier-type of anodic film can be formed by anodizing

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aluminum in neutral solutions ($\text{pH} = 5\text{-}7$) in which the anodic oxide layer stays practically insoluble. These films are extremely thin and dielectrically compact. Porous oxide films are made using strong acid anodizing electrolyte solutions. The laboratory-made AAO membranes are usually prepared by a self-organized two-step anodizing in sulfuric, oxalic and phosphoric acid solutions [2-7].

2. Materials and Experimental Procedure

To obtain nanoporous membranes by anodization the process was carried out on the experimental setup (Figure 1), composed of: electrical source (1), measurement devices (2), thermometer (3), reference electrode (4), Al substrate (5), thermo-insulating outer vessel (6), Cu spiral (7), mechanical stirrer (8), anodizing tank (9), cathode (10).

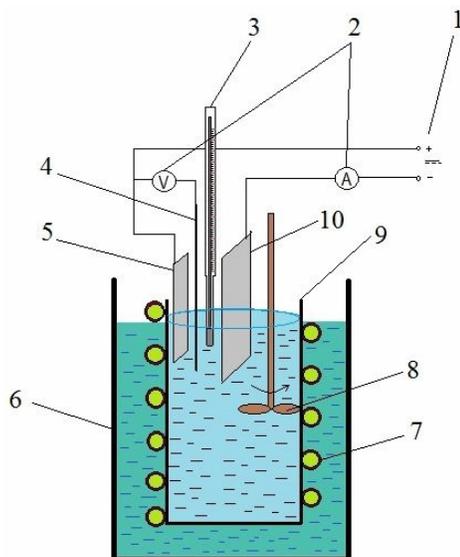


Fig. 1. *Schematic representation of the experimental setup*

The substrate used was a 0.3 mm thick aluminum foil with a working surface of 1.5 cm^2 . To reduce the surface roughness

and for microstructure restoration the starting material was first mechanically polished and then annealed at a temperature of $500 \text{ }^\circ\text{C}$ for one hour. The oxide layer formed in normal conditions on the aluminum surface was removed by a 5% NaOH solution, at $60 \text{ }^\circ\text{C}$ for 1 minute. Subsequently for further reduction of surface roughness, the aluminum foil is electrochemically polished in a 1:4 volume mixture of HClO_4 and $\text{C}_2\text{H}_5\text{OH}$ at a constant current density of 300 mA/cm^2 for one minute at room temperature.

The electrolyte used was 0.3 M $\text{C}_2\text{H}_2\text{O}_4$ solution. First anodization was done at a constant temperature of $5 \text{ }^\circ\text{C}$, varying only the current and anodization time. A Pt grid served as a counter electrode and the distance from the working electrode was 1 cm. For a better homogenization of electrolyte the anodization bath was rigorously stirred. After the first anodization, the formed alumina layer was removed by chemical etching in a mixture of 1.8% CrO_3 and 7.1% H_3PO_4 in distilled water. The aluminum was re-anodized under the same anodizing conditions as those used in the first anodization. In order to obtain the alumina membrane the remaining aluminum substrate was dissolved in saturated HgCl_2 solution. Removal of the barrier layer in a separated anodic alumina membrane, formed by self-organized anodization, was carried out by chemical etching of the oxide. The obtained samples were subjected to a chemical process for opening and enlarging the pores by immersion in a solution of H_3PO_4 .

3. Results and Discussions

The analysis of the oxidic layer was done by scanning electron microscopy (SEM).

Due to the high resistivity of the obtained alumina layer, the samples were gold coated by thermal evaporation.

Anodizing attempts were made at a temperature of 5 °C, in order to reduce dissolution of the formed oxidic layer, maintaining the balance between growth rate of the layer and its dissolution rate. The process was conducted using two current intensities of 100 mA and 200 mA.

First anodization is done in order to obtain a pattern on the aluminum surface that will trigger a well-ordered growth of the alumina oxide layer by the second anodization. Figure 2 presents the structures of the layers obtained in two current densities, after first anodization.

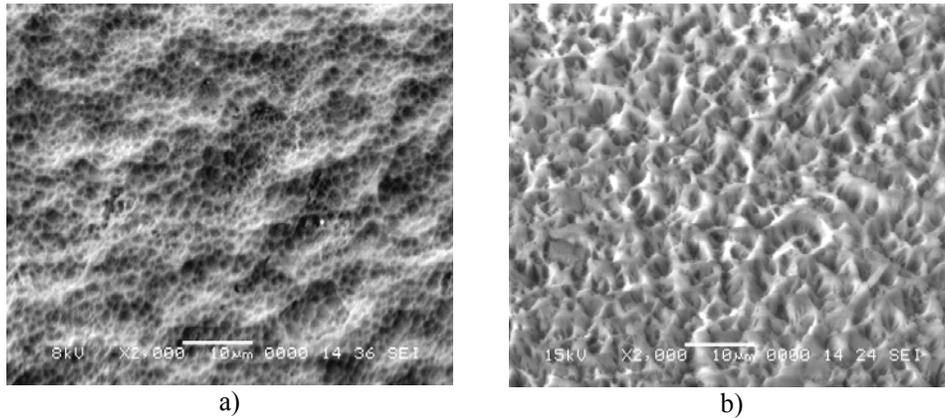


Fig. 2. Oxidic structures obtained by first anodization in oxalic acid: a) $I = 200$ mA; b) $I = 100$ mA

It may be noted that at anodization with a current intensity of 200 mA, a thin oxidic layer was obtained on the sample.

The alumina film reproduces the morphology of the substrate surface. It can also be seen a patterned oxide growth of the alumina layer. Electric field assisted dissolution was higher than the oxidic layer growth at a working current of 200 mA.

At 100 mA the layer is thicker but one cannot observe a greater improvement in ordering of the pattern.

Figure 3 shows the voltage variation with time while working in a galvanostatic regime. The working distance between the two electrodes was 1 cm. Voltage drops sharply at first because of rapid growth of the resistive barrier-type layer.

Equilibrium is reached after 30 minutes, the voltage stabilized at about 15 V. Due to changes in the local current density, small fluctuations around this value are recorded.

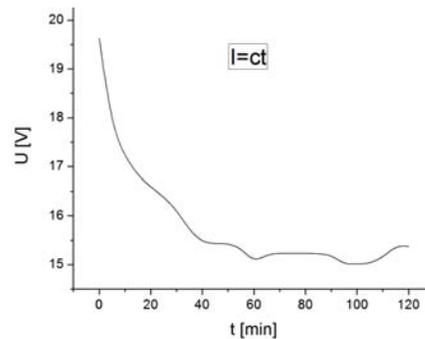


Fig. 3. Voltage variation with time in an anodization process performed at 200 mA

Figure 4 shows the surface morphology and cross section of a sample obtained by a two step anodization method. Current intensity used was 100 mA. In Figure 4a a porous structure can be seen on the sample surface and also the defects in the structure. Figure 4b shows a cross section of the sample in order to highlight uniaxial pore orientation.

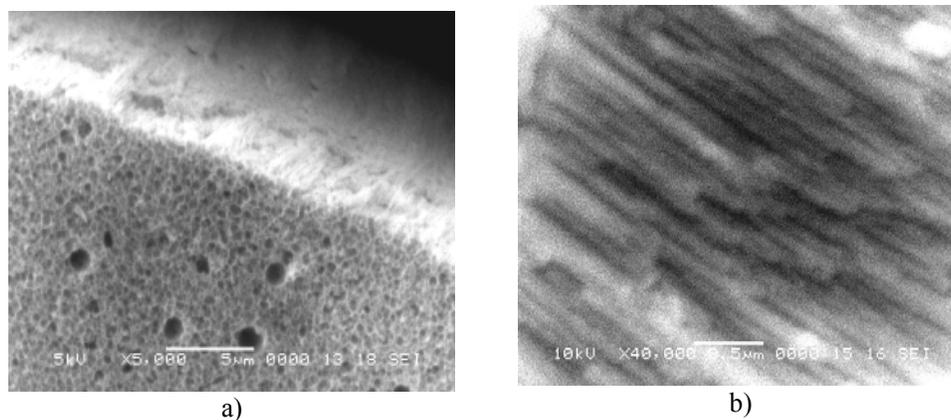


Fig. 4. Oxidic structures obtained by a two step anodization process:
a) sample surface; b) cross section

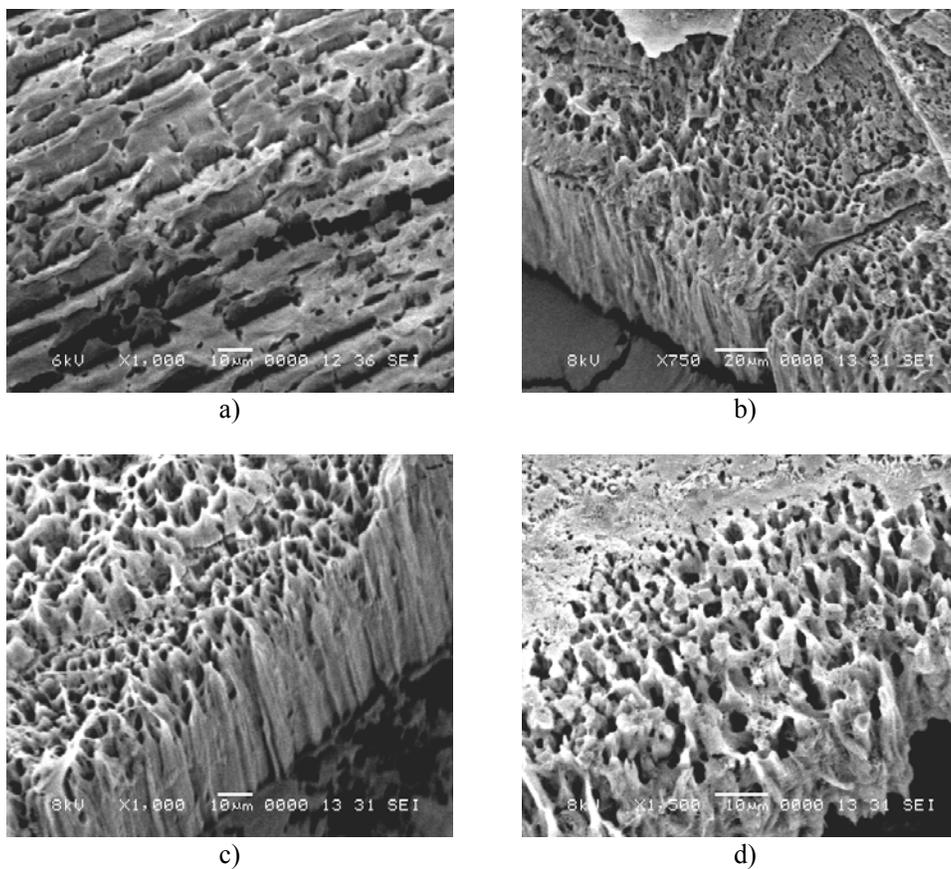


Fig. 5. SEM images of the obtained oxidic layers after chemical treatment in 5% H_3PO_4 :
a) without treatment; b) 15 min H_3PO_4 ; c) 60 min H_3PO_4 ; d) 60 min H_3PO_4

In Figure 5a can be observed the surface morphology of the obtained oxidic layer. This has a residual thin film covering the porous alumina layer. The thin film is continuous and dielectric, which leads to believe that it could be the natural passivation oxide film. Porous anodic alumina layer growth taking place at the metal/oxide interface, will push the existent oxide film towards the electrolyte. After the anodization subsequent operations, were made in order to clean the obtained oxide layer and dissolution of the residual film. The sample was washed in distilled water for 10 minutes, using the same voltage as for the anodizing process. Finally the sample was washed in ethyl alcohol under the same conditions. The obtained film was separated from the Al substrate and chemically treated with 5% H_3PO_4 for one hour, in order to dissolve the residual layer. In Figures 5b, 5c and 5d can be observed that depending on the duration of treatment, dissolution was not uniform. After 15 minutes there was a partial dissolution of the residual layer. A better dissolution is observed after 60 min of chemical treatment (Figure 5c). In some areas the acid attacked the anodic film increasing pore diameter and altering the ordered structure of oxidic layer.

Figure 6 shows a pore cross section. The pore is perpendicular to the surface of

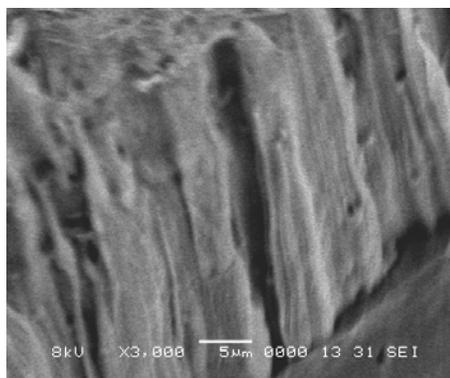


Fig. 6. SEM image of a pore cross section

aluminum substrate. Due to fluctuations in the applied electric field (Figure 3) small variations of pore diameter were recorded on the entire length of the microchannel.

Pores size in the obtained anodic oxide layer is between several hundred nanometers (Figure 4b) to several microns, the largest having a diameter of about 5 micrometers (Figure 6). Figure 7 illustrates more clearly the three layers obtained by anodizing: (1) is the compact residual layer situated on surface of the porous alumina film (2), (3) is the barrier layer after removing the aluminum substrate. It may be noted that the thickness of the two compact layers are much smaller than the porous anodic aluminum oxide film.

Thickness of the alumina porous layer obtained by anodization in 0.3 M oxalic acid at 5 °C for 4 hours, is about 100 micrometers. The current density used to obtain the thickness of the porous layer was 100 mA.

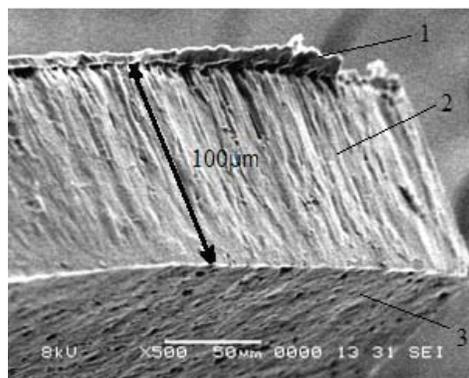


Fig. 7. Structure of the aluminum oxide obtained by a two step anodization process. Thickness of the porous anodic alumina layer

4. Conclusions

The formation of disordered porous alumina by anodization of aluminum has been widely studied in order to protect and decorate the surface of aluminum and to make inorganic membranes.

To obtain ordered porous alumina films, the working temperature was maintained constant at 5 °C. We chose a galvanostatic anodization method, with two current intensities of 100 and 200 mA, respectively.

During the first anodization irregular pores are formed on the aluminum surface. Depending on the anodization time due to repulsive forces between neighboring pores the ordering can occur. Electric field assisted dissolution was higher than the oxidic layer growth at a working current of 200 mA, compared to the sample obtained at 100 mA. This result in different thicknesses of oxide films obtained at various working parameters.

By the second anodization a porous anodic alumina film was obtained. It shows a uniaxial pore orientation perpendicular to the surface of the substrate. A compact residual oxide layer clogs the pores of obtained anodic alumina.

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