

MODEL OF POROUS ALUMINUM OXIDE GROWTH IN THE INITIAL STAGE OF ANODIZATION

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Currently, due to the development of nanotechnology and metamaterials, it has become important to obtain regular self-organized structures, with different parameters. Porous anodic alumina films are self-organizing structures, which can be represented in a hexagonal packing of cylindrical pores normal to the plane of the aluminum film and used as a template for synthesis of various nanocomposites. The diameter of pores and the distance between them can vary (pore diameter — from 2 to 350 nm, the distance between the pores — from 5 to 50 nm), using different electrolytes, voltage and anodizing time. Currently, there are various models that describe the growth of a porous film of aluminum oxide, but none take into account the influence of aluminum layers and electrolyte on the rate of aluminum oxide growth, as well as the effect of surface diffusion. In present work we consider those effects.

Keywords: porous aluminum oxide, anodizing, anodized aluminum oxide.

1. Introduction

Currently the scope of anodic aluminum oxide (AAO) use has expanded beyond corrosion, electrical protection and thermal protection to the development of a template for the synthesis of various nanocomposites. Some examples are: the synthesis of nanotubes via the matrix method [1–4]: where in 50–60 nm thick films, with an ordered system of nanopores (diameter of 40–100 nm) are used for synthesizing oriented carbon nanotubes using pyrolysis of dichloromethane (CH_2Cl_2) under an inert atmosphere of argon at 500 °C, the synthesis of which varies from 6 minutes to 4 hours [5]; the ability to control parameters of the porous structure of Al_2O_3 can be used as filters, carriers for catalysts [1–4]; films with high regularity of the porous structure are increasingly used for creating nanoscale structures in electronic, magnetic, and photonic devices [6]; with sorption of silver ions in the matrix of porous alumina, followed by chemical deposition nanocomposites are synthesized with biochemical activity properties [7].

AAO films consist of a so-called honeycomb structure. This system has a dense hexagonal packing, which is oriented in a perpendicular manner to the substrate surface. In the center of each Al_2O_3 cell, nanoscale pores formed. The bottom surface of the pores is separated from the aluminum substrate by a thin barrier layer. The cells are separated by a so-called honey “Skeleton” [8–13].

The chemical composition of these regions varies and is dependent upon the anodization conditions. The inner part of the cell may include electrolyte anions, where the “skeleton” is made of pure hydrated alumina [11]. The diameter and the distance between them can vary (pore diameter — from 2 to 350 nm, the distance between the pores — from 5 to 50 nm), using different electrolytes, voltage and anodizing times [2, 7].

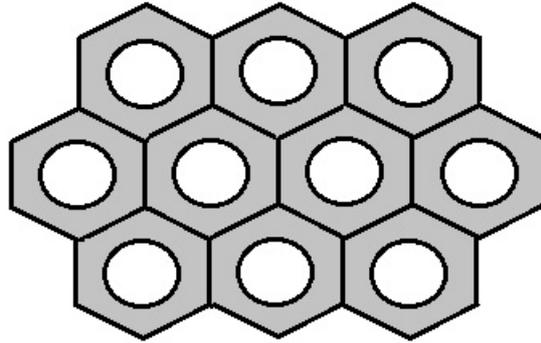


FIG. 1. Hexagonal packing of the porous AAO

2. Anodization technique

On the surface of the aluminum, a non-conductive oxide film is formed that is fairly uniform in its coverage of the aluminum surface (Fig. 2). An electrochemical field is concentrated on surface irregularities of the oxide film and preferentially dissolves the oxide in places where the inhomogeneity is higher. Thus, in areas of inhomogeneity on the surface, pore-growth occurs, increasing with higher temperatures, and with electrical field amplification. Initially, a competition is occurring between adjacent pores, which, after some time, leads to a stabilization of the process and to orderly pore growth [10].

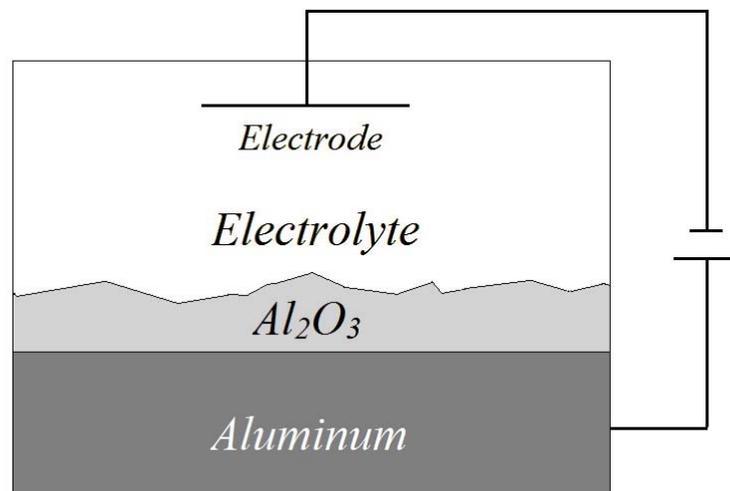


FIG. 2. The process of formation of the porous alumina

In the anodizing process, aqueous solutions of acids moderately dissolve Al₂O₃. The process is carried out in a vessel with an electrolyte, which houses the anode (aluminum) and a cathode (inert conductive material), which are respectively connected to the positive and negative outputs of the power supply (Fig. 2). Thus, the film is formed on the metal, the top layer of which is a micro-porous metal oxide partially hydrated, under which is the bottom layer — anhydrous microscopically thin film of vitreous oxide, featuring a considerable hardness [1–4].

3. Modeling

We considered the motion of the interfaces between the electrolyte- Al_2O_3 (dissolution), and between Al_2O_3 -aluminum (oxidation), as well as the dynamics of moving boundaries and the change of small perturbations of these boundaries. Each area under Laplace's equation is solved for the potential of the electric field. The growth process of the porous alumina is described by the theory of small perturbations. In zero approximation boundaries are considered flat and the speed of their movements is proportional to the current density at these boundaries. In the first approximation, small perturbations of the interface are considered, which lead to small changes in the potential and the current on these boundaries. The evolution of small perturbations of the interface is defined as a disturbance of the current density at the borders, and the process of surface diffusion.

3.1. The evolution of perturbations of the film boundaries of Al_2O_3 -layer model (Figure 3):

Fig. 3 shows the geometry of the area under consideration. Here h_1 and h_2 are small perturbations of the Al- Al_2O_3 and Al_2O_3 -electrolyte boundaries, respectively.

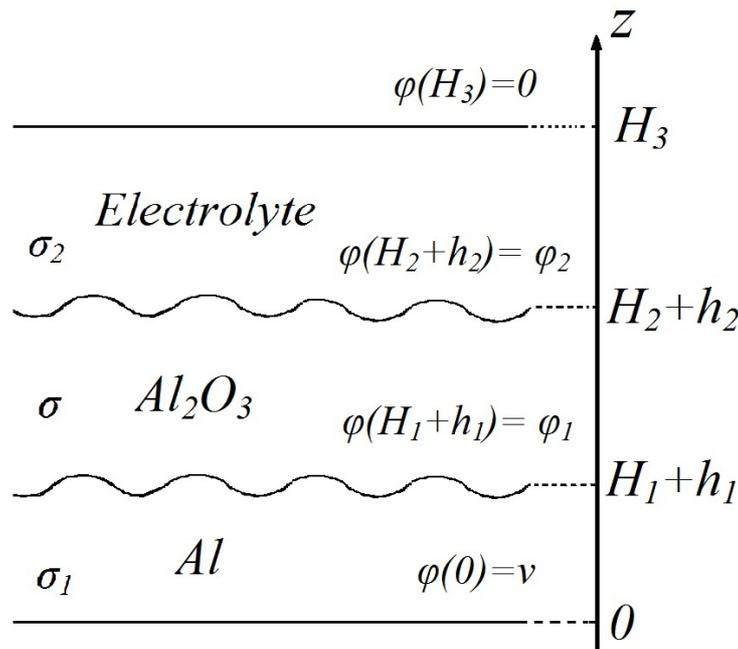


FIG. 3. Inhomogeneous film with rough boundaries

We present the results of potentials perturbation calculations in each layer [14–16]:
 In the aluminum layer:

$$\hat{\phi}_{\vec{k}} = \left(\hat{\phi}_1 + \frac{v}{\sigma_1 \vartheta} h_{1\vec{k}} \right) \frac{sh(kz)}{sh(kH_1)}.$$

In the electrolyte layer:

$$\hat{\phi}_{\vec{k}} = \left(\hat{\phi}_2 + \frac{v}{\sigma_2 \vartheta} h_{2\vec{k}} \right) \frac{sh(k(z - H_3))}{sh(k(H_2 - H_3))}.$$

In the aluminum oxide layer:

$$\hat{\phi}_{\vec{k}} = \frac{1}{sh(kH)} \left(\left(\hat{\phi}_{2\vec{k}} + \frac{v}{\sigma\vartheta} h_{2\vec{k}} \right) sh(k(z - H_1)) - \left(\hat{\phi}_{1\vec{k}} + \frac{v}{\sigma\vartheta} h_{1\vec{k}} \right) sh(k(z - H_2)) \right),$$

where $\hat{\phi}_{\vec{k}}$ — the Fourier transform of the potential disturbance to the coordinates x, y :

$$\hat{\phi}_{\vec{k}} = \int_{-\infty}^{\infty} e^{-ik_y y} \int_{-\infty}^{\infty} \hat{\phi} e^{-ik_x x} dx dy, k^2 = k_x^2 + k_y^2, \phi = \phi_{(z)}^0 + \hat{\phi}, \phi_{(z)}^0 — stationary potential$$

for the homogeneous problem, $\hat{\phi}$ — potential oscillations, ϕ_1 — electrostatic potential of the aluminum layer on Al-Al₂O₃ interface, ϕ_2 — electrostatic potential of the aluminum layer on electrolyte-Al₂O₃ interface, σ_1 — conductivity of the aluminum, σ — conductivity of aluminum-oxide, σ_2 — conductivity of the electrolyte, $\vartheta = \left(\frac{H}{\sigma} + \frac{H_1}{\sigma_1} + \frac{H_3 - H_2}{\sigma_2} \right)$, v — anodization voltage, H — thickness of aluminum oxide, $H_1 + h_1$ — thickness of the aluminum layer, $H_3 - (H_2 + h_2)$ — thickness of the electrolyte layer, $h_{1\vec{k}} = \int_{-\infty}^{\infty} e^{-i(k_y y)} \int_{-\infty}^{\infty} e^{-i(k_x x)} h_1 dx dy$,

$$h_{2\vec{k}} = \int_{-\infty}^{\infty} e^{-i(k_y y)} \int_{-\infty}^{\infty} e^{-i(k_x x)} h_2 dx dy.$$

Using conditions of continuity of the current density at both interfaces, we obtain the system of equations relating the potential disturbance on the interfaces:

$$\begin{cases} (-\sigma_2 sh(kH) - \sigma ch(kH)) \hat{\phi}_{2\vec{k}} + \sigma \hat{\phi}_{1\vec{k}} = \beta e^{kH} - \alpha \\ -\sigma \hat{\phi}_{2\vec{k}} + (\sigma_1 sh(kH) + \sigma ch(kH)) \hat{\phi}_{1\vec{k}} = \beta - \alpha e^{kH} \end{cases} \quad (1)$$

where $\alpha = \frac{v}{\vartheta} h_{1\vec{k}}, \beta = \frac{v}{\vartheta} h_{2\vec{k}}$.

We consider the solutions of the system (1) for different values kH :

I. For $kH \ll 1$,

$$\begin{cases} \hat{\phi}_{1\vec{k}} = 0 \\ \hat{\phi}_{2\vec{k}} = \frac{(\alpha - \beta)\sigma_1}{\sigma_1 \sigma_2 kH + \sigma_1 \sigma + \sigma_2 \sigma} \end{cases} .$$

II. For $kH \gg 1$,

$$\begin{cases} \hat{\phi}_{1\vec{k}} = 0 \\ \hat{\phi}_{2\vec{k}} = \frac{2}{\sigma_2} \left(\frac{\alpha}{e^{kH}} - \beta \right) \end{cases} .$$

3.2. Calculation of the evolution of alumina boundaries perturbations, without consideration of surface diffusion

The rate of change of small perturbations of the Al-Al₂O₃ and Al₂O₃-electrolyte boundaries without the influence of surface diffusion is proportional to the perturbation of the current density at these interfaces $\frac{dh}{dt} = a\sigma \frac{\partial \phi}{\partial z}$.

For Al-Al₂O₃ interface:

$$\frac{\partial \hat{\phi}_{\vec{k}}}{\partial z} = k \left(\hat{\phi}_1 + \frac{v}{\sigma_1 \vartheta} h_{1\vec{k}} \right) \frac{ch(kz)}{sh(kH_1)}.$$

Then:

$$\frac{dh_{1\vec{k}}}{dt} = \left(\frac{a_1 v k}{\vartheta} h_{1\vec{k}} \right) cth(kH_1), \quad h_{1\vec{k}}(t) = h_{1\vec{k}}(0) \cdot e^{\frac{a_1 k v \cdot cth(kH_1)}{\vartheta} t}. \quad (2)$$

For the Al₂O₃-electrolyte interface:

$$\frac{\partial \hat{\phi}_{\vec{k}}}{\partial z} = k \left(\hat{\phi}_2 + \frac{v}{\sigma_2 \vartheta} h_{2\vec{k}} \right) cth(kH) \quad (3)$$

We consider two cases:

I. When $kH \ll 1$,

Since the conductivity of the electrolyte and alumina is small compared with aluminum, we obtain from (3):

$$h_{2\vec{k}} = h_{1\vec{k}}(0) \cdot e^{\frac{a_1 kv}{\vartheta} t} + \left(h_{2\vec{k}}(0) - h_{1\vec{k}}(0) \right) e^{-\frac{a_2 kv}{\vartheta} t} \quad (4)$$

II. When $kH \gg 1$,

$$h_{2\vec{k}} = \frac{2h_{1\vec{k}}(0) a_2 e^{\frac{a_1 kv}{\vartheta} t}}{(a_1 + a_2) e^{kH}} + \left(h_{2\vec{k}}(0) - \frac{2h_{1\vec{k}}(0) a_2}{(a_1 + a_2) e^{kH}} \right) e^{-\frac{a_2 kv}{\vartheta} t}. \quad (5)$$

From (4-5), we see that in this approximation, the perturbation on the Al_2O_3 -electrolyte interface increases indefinitely with time.

3.3. Calculation of the evolution of alumina boundaries perturbations, with consideration of surface diffusion

The rate of change of small perturbations of the Al- Al_2O_3 and Al_2O_3 -electrolyte boundaries with the influence of surface diffusion is described by the relation $\frac{\partial h}{\partial t} = V + D\Delta^2 h$, where D — is the surface diffusion coefficient.

For the Al- Al_2O_3 interface:

$$V_1 = \left(\frac{a_1 v}{\vartheta} h_{1\vec{k}} \right),$$

$$\frac{dh_{1\vec{k}}}{dt} = h_{1\vec{k}} \left(\frac{a_1 v k}{\vartheta} - D_1 k^4 \right), h_{1\vec{k}} = h_{1\vec{k}}(0) e^{\left(\frac{a_1 v k}{\vartheta} - D_1 k^4 \right) t}. \quad (6)$$

From (6), we get the value of spectral parameter corresponding to the limit of stability for the Al- Al_2O_3 interface:

$$k_1 = \left(\frac{a_1 v}{\vartheta D_1} \right)^{1/3}. \quad (7)$$

All perturbations of this interface with $k < k_1$ are unstable. Perturbations of the upper boundary in this spectral interval are the source of pore formation. We will estimate of distance between centers of aluminum oxide pores as $2\pi/k_1$.

For the Al_2O_3 -electrolyte interface:

For $kH \ll 1$,

$$V_2 = \frac{v k a_2}{\vartheta H} \left(h_{1\vec{k}}(0) \cdot e^{\frac{a_1 kv \cdot c t h(kH_1)}{\vartheta} t} - h_{2\vec{k}} \right). \quad (8)$$

For $kH \gg 1$,

$$V_2 = \sigma_2 k a_2 \left(\frac{2}{\sigma_2} \left(\frac{\alpha}{e^{kH}} - \beta \right) + \frac{v}{\sigma_2 \vartheta} h_{2\vec{k}} \right). \quad (9)$$

Then, as in (7-8), we obtain the expression, taking into account the surface diffusion:

For $kH \ll 1$,

$$h_{2\vec{k}} = h_{1\vec{k}}(0) \cdot e^{\left(\frac{a_1 kv}{\vartheta} - D_2 k^4 \right) \cdot t}. \quad (10)$$

For $kH \gg 1$,

$$h_{2\vec{k}} = \frac{2h_{1\vec{k}}(0) a_2 e^{\left(\frac{a_1 kv}{\vartheta} - D_2 k^4 \right) \cdot t}}{(a_1 + a_2) e^{kH}}. \quad (11)$$

From (10–11), we get the value of spectral parameter corresponding to the limit of stability for the Al_2O_3 -electrolyte interface:

$$k_2 = \left(\frac{a_1 v}{\vartheta D_2} \right)^{1/3}. \quad (12)$$

All perturbations of this interface with wavelength $k < k_2$ are unstable. The evolution of perturbations in this spectral interval determines the imperfection of the porous structure. This should be considered when preparing the aluminum plate used in this process.

4. Conclusion

As a result of the developed model, we obtained the minimum distance $2\pi \left(\frac{\vartheta D_1}{a_1 v} \right)^{1/3}$ between centers of aluminum oxide pores in the beginning of anodizing process. The irregularities of the porous structure contains in the spectral interval $k_2 < \left(\frac{a_1 v}{\vartheta D_2} \right)^{1/3}$.

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