Model of porous aluminium oxide growth during initial stage of anodization

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Abstract. Currently, the development of nanotechnology and metamaterials requires the ability to obtain regular self-assembled structures with different parameters. One such structure is porous alumina in which the pores grow perpendicular to the substrate and are hexagonally packed. Pore size and the distance between them can be varied depending on the anodization voltage, the electrolyte and the anodization time (pore diameter - from 2 to 350 nm, the distance between the pores - from 5 to 50 nm). At the moment, there are different models describing the process of anodizing aluminum, in this paper we propose a model that takes into account the effect of layers of aluminum, aluminum oxide, and the electrolyte, as well as the influence of the effect of surface diffusion.

1. Introduction

Currently the scope of anodic aluminum oxide (AAO) use expanded from protection against corrosion, electrical protection, and thermal protection to a development of a template for the synthesis of various nanocomposites. Such as: synthesizing nanotubes with matrix method [1-2]: 50-60 nm thick films, with an ordered system of nanopores (diameter of 40-100 nm) is used for synthesizing oriented carbon nanotubes [3]; the ability to control parameters of the porous structure of Al₂O₃ can be used as filters, carriers for catalysts [2]; films with high regularity of the porous structure are increasingly used for creating nanoscale structures in electronic, magnetic, and photonic devices [4]; with sorption of silver ions in the matrix of porous alumina, followed by chemical deposition nanocomposites are synthesized with biochemical activity properties [5].

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 (Figure 1).

Figure 1. Hexagonal packing of the porous AAO
2. Model

In this paper we consider the motion of the interfaces between the electrolyte-Al₂O₃ (dissolution), and between Al₂O₃-aluminum (oxidation), as well as consider the dynamics of moving boundaries and the change of small perturbations of these boundaries. In 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 first approximation small perturbations of the interface are considered, which lead to small changes in potential and 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.

2.1. The evolution of perturbations of the film boundaries of Al₂O₃-layer model:

Figure 2 shows the geometry of the area under consideration. Here h₁ and h₂ are small perturbations of the boundaries of Al-Al₂O₃ and Al₂O₃-electrolyte, respectively.

![Figure 2. Inhomogeneous film with rough boundaries.](image)

Using conditions of continuity of the current density at both interfaces (aluminum-alumina, alumina-electrolyte) we obtain the system of equations relating the potential disturbance on the interfaces:

\[
\begin{align*}
\left\{ -\sigma_1 sh(kH) - \sigma ch(kH) \right\} \hat{\phi}_{2k} + \sigma \hat{\phi}_{ik} &= \beta e^{ih} - \alpha \\
-\sigma \hat{\phi}_{2k} + (\sigma_1 sh(kH) + \sigma ch(kH)) \hat{\phi}_{ik} &= \beta - \alpha e^{ih}
\end{align*}
\]

(1)

where \(\alpha = \frac{v}{\partial_x} h_{1k}, \beta = \frac{v}{\partial_y} h_{2k}, \hat{\phi}_k\) - the Fourier transform of the potential disturbance to the coordinates \(x, y\), \(\hat{\phi}_k = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \hat{\phi} \exp(-ik_x x) \exp(-ik_y y) dx dy, k^2 = k_x^2 + k_y^2, \varphi = \varphi_{(z)} + \hat{\varphi}, \varphi_{(z)}\) - stationary potential for the homogeneous problem, \(\varphi\) - potential oscillations, \(\varphi_1\) - electrostatic potential of the aluminum layer on Al-Al₂O₃ interface, \(\varphi_2\) - electrostatic potential of the aluminum layer on electrolyte-Al₂O₃ interface, \(\sigma_1\) - conductivity of the aluminum, \(\sigma\) - conductivity of aluminum oxide, \(\sigma_2\) - conductivity of the electrolyte, \(v\) - 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, $h_{1i} = \int \exp(-ik_y y) \int \exp(-ik_x x) h_i dx dy$, $h_{2i} = \int \exp(-ik_y y) \int \exp(-ik_x x) h_i dx dy$.

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

I. For $kH \ll 1$

\[
\begin{align*}
\dot{\phi}_{1i} &= 0 \\
\dot{\phi}_{2i} &= \frac{(\alpha - \beta) \sigma_1}{\sigma_2 \sigma_3 kH + \sigma_2 \sigma + \sigma_3 \sigma}
\end{align*}
\]

II. For $kH \gg 1$

\[
\begin{align*}
\dot{\phi}_{1i} &= 0 \\
\dot{\phi}_{2i} &= \frac{2 \alpha}{\sigma_2} \left( e^{ikx} - \beta \right)
\end{align*}
\]

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

The rate of change of small perturbations of the boundaries Al-Al$_2$O$_3$ and Al$_2$O$_3$-electrolyte without the influence of surface diffusion is proportional to the perturbation of the current density at these interfaces $\frac{dh_i}{dt} = a \sigma \frac{\partial \phi}{\partial z}$.

For Al-Al$_2$O$_3$ interface:

\[
h_{1i}(t) = h_{1i}(0) \cdot \exp \left( \frac{a_{1i} k v \cdot cth( kH_1 t)}{\vartheta} \right)
\]

(2)

For Al$_2$O$_3$-electrolyte interface we consider two cases

I. When $kH \ll 1$

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

\[
h_{2i} = h_{1i}(0) \cdot \exp \left( \frac{a_{2i} k v}{\vartheta} t \right) + \left( h_{1i}(0) - h_{2i}(0) \right) \exp \left( -\frac{a_{2i} k v}{\vartheta} t \right)
\]

(3)

II. When $kH \gg 1$

\[
h_{2i} = \frac{2 h_{1i}(0) a_{2i} \exp \left( \frac{a_{2i} k v}{\vartheta} t \right)}{a_1 + a_2 e^{ikx}} + \left( h_{2i}(0) - \frac{2 h_{2i}(0) a_{2i}}{(a_1 + a_2) e^{ikx}} \right) \exp \left( -\frac{a_{2i} k v}{\vartheta} t \right)
\]

(4)

From (3-4) we see, that in this approximation, the perturbation on the interface of Al$_2$O$_3$-electrolyte increases indefinitely with time.

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

The rate of change of small perturbations of the interfaces Al-Al$_2$O$_3$ and Al$_2$O$_3$-electrolyte with the influence of surface diffusion is described by the relation $\frac{\partial h_i}{\partial t} = V + D \Delta^2 h_i$, where $D$ – is the surface diffusion coefficient.
For Al-Al₂O₃ interface:

\[ V_i = \left( \frac{a_i v}{\vartheta} h_{1k} \right) \]

\[ h_{1k} = h_{1k}^{(0)} \exp \left( \left( \frac{a_i v k}{\vartheta} - D_{k^4} \right) t \right) \]

From (5) we get the wavelength corresponding to the limit of stability for Al-Al₂O₃ interface (figure 3):

\[ \lambda_i = 2\pi \sqrt{\frac{\partial D}{a_i v}}. \]

All perturbations of this interface with wavelength \( \lambda > \lambda_i \) are unstable.

![Figure 3](image)

Figure 3. Change of the wavelength corresponding to the limit of stability with anodization voltage

For Al₂O₃-electrolyte interface:

For \( kH << 1 \)

\[ V_2 = \frac{vka_z}{\vartheta H} \left( h_{1k}^{(0)} \cdot \exp \left( \frac{a_i k v \cdot \cosh \left( kH_{2k} \right)}{\vartheta} t \right) - h_{2k}^{(0)} \right) \]

(7)

For \( kH >> 1 \)

\[ V_2 = \sigma_2^2 k a_z \left( 2 \frac{\sigma_2}{e^{\alpha}} - \beta + \frac{\vartheta}{\sigma_2 \vartheta} h_{2k}^{(0)} \right) \]

(8)

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

For \( kH << 1 \)

\[ h_{2k} = h_{1k}^{(0)} \cdot \exp \left( \left( \frac{a_i k v}{\vartheta} - D_{k^4} \right) \cdot t \right) \]

(9)

For \( kH >> 1 \)

\[ h_{2k} = \frac{2h_{1k}^{(0)} a_2}{(a_1 + a_2) e^{\alpha}} \cdot \exp \left( \left( \frac{a_i k v}{\vartheta} - D_{k^4} \right) \cdot t \right) \]

(10)
From (9-10) we get the wavelength corresponding to the limit of stability for $\text{Al}_2\text{O}_3$-electrolyte interface:

$$\lambda_2 = 2\pi \sqrt{\frac{\vartheta D_2}{a_1 k_\vartheta}}. \tag{11}$$

All perturbations of this interface with wavelength $\lambda > \lambda_2$ are unstable.

We assume that surface diffusion coefficient $D_2$ on the $\text{Al}_2\text{O}_3$-electrolyte interface is larger than the same coefficient $D_1$ on the Al-$\text{Al}_2\text{O}_3$ interface. According to (6), (11), the correspondent critical wavelengths satisfy of inequality $\lambda_2 < \lambda < \lambda_1$. Therefore, for perturbations with wavelength $\lambda$ in interval $\lambda_2 < \lambda < \lambda_1$ the upper boundary of alumina layer is unstable and bottom boundary is stable. The perturbations of upper boundary in this interval of wavelength are the source of porous formation. For wavelength $\lambda > \lambda_1$ the bottom boundary of alumina is unstable. The evolution of perturbations in this wavelength region determines the irregularities of porous structure.

3. Conclusion
In this work we consider the solutions of the system (1) for different values $kH$. And add the influence of surface diffusion on the process.

As a result of the developed model we obtained the minimum distance $2\pi (\vartheta D_2/a_1) \frac{1}{3}$ between centres of alumina pores in the beginning of anodizing process. The irregularities of porous structure contains in the spectral interval $k_2 < (a_1 k_\vartheta/\vartheta D_2)^{\frac{1}{3}}$.

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