Modelling the growth process of porous aluminum oxide film during anodization

E M Aryslanova[1], A V Alfimov[1], S A Chivilikhin[1]

[1]ITMO University, Kronverkskiy Ave, 49, St. Petersburg, 197101, Russia

E-mail: elizabeth.aryslanova@gmail.com

Abstract. Currently it has become important for the development of metamaterials and nanotechnology to obtain regular self-assembled structures. One such structure is porous anodic alumina film that consists of hexagonally packed cylindrical pores. In this work we consider the anodization process, our model takes into account the influence of layers of aluminum and electrolyte on the rate of growth of aluminum oxide, as well as the effect of surface diffusion. In present work we consider those effects. And as a result of our model we obtain the minimum distance between centers of alumina pores in the beginning of anodizing process.

1. Introduction

Currently, the development of nanotechnology and metamaterials requires the ability to obtain regular self-assembled structures with different parameters [1-2]. One such structure is porous alumina film, which are self-organizing structures that consist of hexagonally packed cylindrical pores (Figure 1). Artificially on the surface of the aluminum may be built a thick layer of porous aluminum oxide film. Highly ordered pores may be obtained using two-stage anodization process, proposed in 1995 by Masuda et al. [3]. 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).

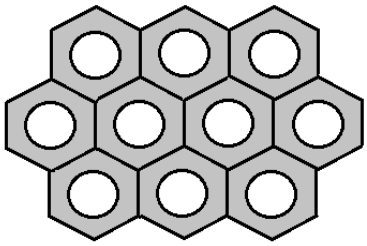

Figure 1. Hexagonal packing of the porous AAO

Anodizing is carried out in a vessel with electrolyte (aqueous solution of acid: oxalic, phosphoric acid; chromium, etc.), where are placed anode (aluminum) and cathode (inert conductive material), which are respectively connected to the positive and negative power supply output (Figure 2).

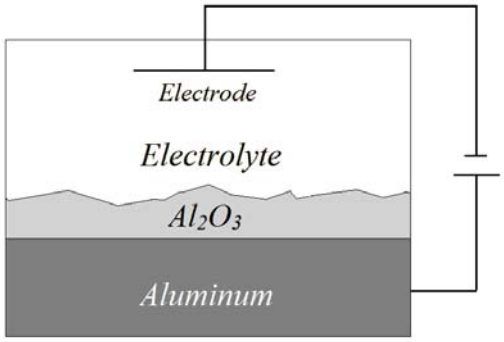

Figure 2. Anodizing process

On the surface of the aluminum grows thin aluminum oxide film. As an electric current flows at the aluminum - electrolyte border there grows a thin dense electrolyte film – barrier layer. Barrier layer grows due to the migration of aluminum ions towards oxygen ions. The thickness of this barrier layer (0.01 – 0.1 nm) does not change throughout the process as it dissolves at the outer side exposed to the electrolyte [4].

Electrochemical field localizes on inhomogeneities of the surface of oxide, therefore the oxide dissolves more intense the higher the inhomogeneity of the field. Growth then occurs in the area of inhomogeneity. After some time the competition between the pores leads to a stabilization process. However, the thicker the structure, the more uneven grows the pore walls. Alumina layer is then dissolved, leaving a regular array of porous aluminum. The whole anodizing process is repeated a second time, which leads to growth of regular porous alumina.

2. Model

In this paper we describe an analytical model of the growth of anodic alumina. We consider the motion of the interfaces between the electrolyte-Al_2O_3 (dissolution) and between the Al_2O_3-aluminum (oxidation) (Figure 2).

We consider the dynamics of moving boundaries and the change of small perturbations forms of these boundaries. In each of the areas under consideration Laplace equation for the electric potential is solved. The process of growth of porous alumina is described by the theory of small perturbations. In zero approximation boundaries are considered flat and the speed of their movement proportional to the current density at these boundaries. The first approximation takes into account the small perturbations of the interface, which lead to small changes in the potentials and currents at these boundaries. The evolution of small perturbations of the interface is defined as a perturbation of the current density at the borders, and the process of surface diffusion.

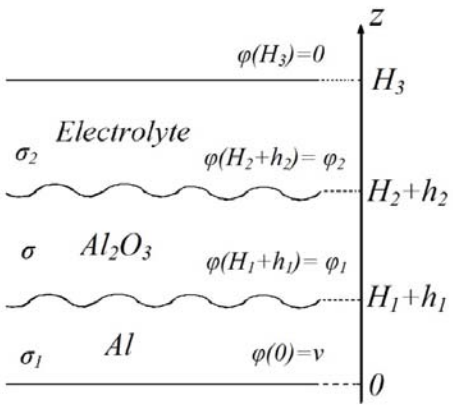

Figure 3. Inhomogeneous film with rough boundaries.

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

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

where $\alpha=(v/\vartheta)h_{1\vec{k}}$, $\beta=(v/\vartheta)h_{2\vec{k}}$. $\hat{\varphi}_{\vec{k}}$ - the Fourier transform of the potential disturbance to the coordinates x, y, $\varphi=\varphi^0_{(z)}+\hat{\varphi}$, $\varphi^0_{(z)}$ - stationary potential for the homogeneous problem, $\hat{\varphi}$ - potential oscillations, $_1$ – electrostatic potential of the aluminum layer on Al-Al_2O_3 interface, $_2$ – electrostatic potential of the aluminum layer on electrolyte-Al_2O_3 interface, $_1$ – conductivity of the aluminum, – conductivity of aluminum oxide, $_2$ – conductivity of the electrolyte, $\vartheta=\left(H/\sigma+H_1/\sigma_1+\left(H_3-H_2\right)/\sigma_2\right)$, 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 electrolyte, $h_{1\vec{k}}=\int_{-\infty}^{\infty}\exp\left[-ik_y y\right]\int_{-\infty}^{\infty}\exp\left[-ik_x x\right]h_1 dxdy$, $h_{2\vec{k}}=\int_{-\infty}^{\infty}\exp\left[-ik_y y\right]\int_{-\infty}^{\infty}\exp\left[-ik_x x\right]h_2 dxdy$.

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

The rate of change of small perturbations of the boundaries Al-Al_2O_3 and Al_2O_3-electrolyte without the influence of surface diffusion is proportional to the perturbation of the current density at these interfaces $dh/dt=a\sigma\, d\varphi/dz$. Since the conductivity of the electrolyte and alumina is small compared with aluminum we see that the perturbation on the interface of Al_2O_3-electrolyte increases indefinitely with time.

The rate of change of small perturbations of the interfaces Al-Al_2O_3 and Al_2O_3-electrolyte 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 Al-Al_2O_3 interface we get the wavelength corresponding to the limit of stability:

$$\lambda_1=2\pi\sqrt[3]{a_1 v/\vartheta D_1}. \quad (2)$$

All perturbations of this interface with wavelength $\lambda>\lambda_1$ are unstable.

For Al_2O_3-electrolyte interface we get the wavelength corresponding to the limit of stability:

$$\lambda_2=2\pi\sqrt[3]{a_1 v/\vartheta D_2}. \quad (3)$$

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

We assume that surface diffusion coefficient D_2 on the Al_2O_3-electrolyte interface is larger than the same coefficient on D_1 the Al-Al_2O_3 interface. According to (2), (3), the correspondent critical wavelength satisfies of inequality $\lambda_2<\lambda_1$. Therefore, for perturbations with wavelength λ 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

As a result of the developed model we obtained the minimum distance $2\pi\sqrt[3]{a_1 kv/\vartheta D_2}$ between centres of aluminum oxide pores in the beginning of anodizing process. The irregularities of porous structure have wavelength $\lambda > 2\pi\sqrt[3]{a_1 kv/\vartheta D_1}$. The dependence of distance between centres of inhomogeneities on anodizing voltage is shown in Figure 4. It follows that the bigger the anodizing voltage, the less smooth the surface should be at the beginning of anodization process.

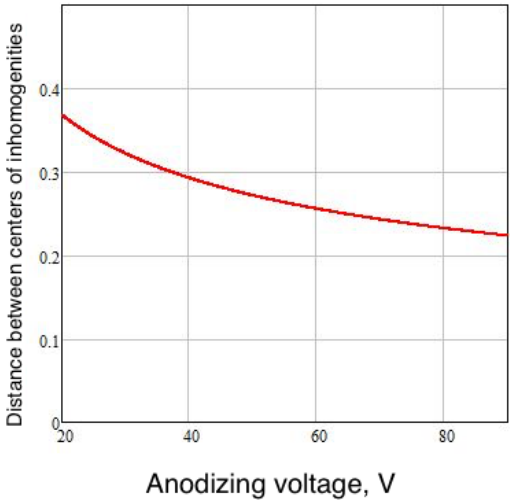

Figure 4. Dependence of distance between centres of inhomogeneities on anodizing voltage

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References

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