

Pore formation in highly ordered anodic alumina templates controlled by the rate of electrolyte stirring at the oxide surface

V. Videkov¹, I. Vrublevsky², B. Tzaneva¹, K. Chernyakova³

¹Technical University of Sofia, St. Kl. Ohridski Blvd 8, 1000 Sofia, Bulgaria

²Belarussian State University of Informatics and Radioelectronics, P.Brovki 6, 220013 Minsk, Belarus

³State research institute Center for Physical Sciences and Technology, Savanorių ave. 231, LT-02300 Vilnius, Lithuania

videkov@tu-sofia.bg, vrublevsky@bsuir.edu.by, borianatz@tu-sofia.bg, katsiaryna.charniakova@fmnc.lt

Abstract – This paper presents the studies on the cooling of the aluminum surface during its anodization by controlling the rate of electrolyte stirring and its effect on the morphology of the nanoporous anodic films. The obtained data demonstrates the possibility to control the pore diameter during the anodizing process without changing the anodizing voltage and interpore distance. This allows a higher utilization factor of the anode oxide when it is used as a matrix to obtain metal nanowires.

Keywords – anodic oxide template; copper nanocomposite; copper nanowires; fluxes, transmission spectrum.

I. INTRODUCTION

Anodic alumina is widely used as a matrix for the manufacture of metal nanowires using electrochemical filling of nanopores [1]. The pores in the oxide matrix can be filled with various metals, and the oxide thickness, as a rule, determines the length of nanowires [2]. The diameter of the nanowires depends on the diameter of the oxide matrix nanopores [3]. If larger diameter metal wires are required, a higher anodizing potential is used. At the same time, the ratio between the interpore distance and the pore diameter for oxide matrices remains practically constant [4]. This means that the yield of the mass of the metal wire (\mathcal{E}) to the unit area will also be a constant value:

$$\mathcal{E} = (N \pi d^2)/4 \quad (1)$$

where N is the number of pores per unit area; d is pore diameter, nm. Consequently, if the pore diameter is increased, then the amount of metal deposited per unit area will increase too.

It is known for anodizing processes that increasing the temperature of the aluminum substrate, the pore diameter of the formed Al_2O_3 films increases too [5]. This can also lead to an acceleration of dissolution of the pore walls and, consequently, to an increase in the pore diameter. This process can be controlled by cooling the plate holder [6] or by controlling the temperature of the electrolyte. It should be noted that when the electrolyte temperature is high enough, it may be difficult to maintain the required temperature dynamics due to the large volume of electrolyte in the electrochemical cell and its thermal inertness. Therefore, the problem of obtaining a higher electrolyte temperature at the oxide-aluminum interface and at the same time a lower electrolyte temperature in the cell volume is relevant for aluminum anodizing processes

[5]. Since anodizing is an exothermic process, then at a constant potential, the anodizing current strongly depends on the temperature and the rate of the electrolyte. The effect of temperature has been the subject of many researches, while the rate of electrolyte stirring is usually not even mentioned.

This paper studies the effect of the cooling of aluminum surface during its anodization by controlling the rate of electrolyte stirring.

II. EXPERIMENTAL PART

Aluminum foil with technical grade purity (99.5%) and thickness 100 μm was used. The test specimens were made in the shape of a boat (Fig. 1-a). The anodization process was accomplished in 600 mL of 1.0 M phosphoric acid solution at 150 V as samples were allowed to float on the electrolyte as shown in Figure 1-b. The electrolyte temperature varied from 1.8 to 7.0 $^\circ\text{C}$.

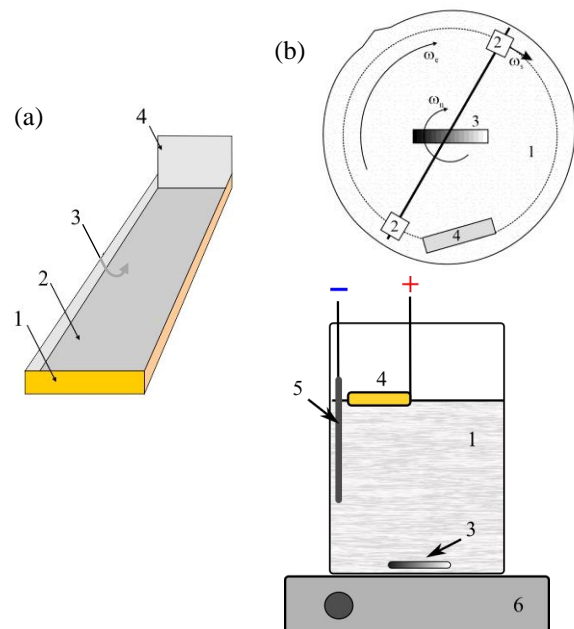


Fig. 1. Scheme of the experimental setup: (a) aluminum sample in the shape of a boat: 1 – the outside board of the boat, coated with varnish, 2 – the upper surface of the boat, for which the temperature was measured, 3 – the anodized under side of the boat, 4 – the narrow boat wall used for electrical contact;

(b) top and side view of the electrochemical cell: 1 – electrolyte, 2 - pieces of styrofoam fixed with a rod; 3 - magnetic stirrer bar; 4 – boat sample; 5 – stainless steel cathode; 6 – magnetic stirrer.

Experiments on measuring the temperature of the aluminum substrate were carried out for different rotation rates of the stirrer and were recalculated in linear speed for the average radius on which the aluminum boat was located (Fig. 2-b). The electrolyte speed was 7.5, 109, and 382 mm s⁻¹. The determination accuracy was 3.5% in terms of velocity and 7% in terms of location.

The temperature of the aluminum sample (T_{Al-IR}) was measured from the upper side of the aluminum foil using IR. To ensure a stable emissivity, this surface of the foil was covered with a thin layer of hydrophilic oxide and wetted with a thin layer of water. In this case, the emissivity of the coating was close to the value of a black body.

The temperature in the electrolyte volume (T_{E-Hg}) in the electrochemical cell was controlled with an accuracy of ± 0.1 °C using a mercury thermometer (integrating rapid changes). A thermal imaging camera (FLIR camera) was used to monitor the temperature of the upper side of the aluminum foil (T_{Al-IR}) as well as the temperature at electrolyte-air interface (T_{E-IR}). Before the beginning of the anodizing process, the temperature of the electrolyte and foil was determined. In this case, the electrolyte was not stirred and the anodizing voltage was not applied to the sample. The surface morphology of anodized samples was observed by scanning electron microscopy (SEM).

Some of the samples were used as a matrix to obtain copper nanowires. For this purpose, first the barrier layer at the oxide-aluminum interface was dissolved electrochemically and then an electrochemical deposition of copper from an electrolyte containing 0.5 M copper sulfate was conducted at constant cell voltage of 0.3 V.

III. RESULTS AND DISCUSSION

The dependence of the anodic current density on temperature for the process of anodizing aluminum is presented in Fig. 2. It was found that with a decrease in the stirring rate, the anodizing current increases, while the electrolyte temperature does not change significantly. At a lower stirring speed, the current density increases. However, this leads to instability of the temperature control process.

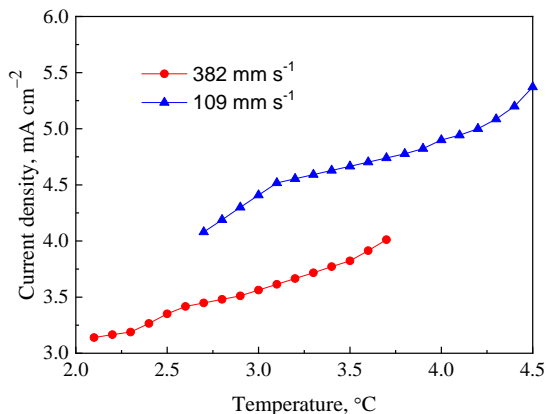


Fig. 2. Change in the anodizing current density depending on the temperature of the electrolyte at flow rates 109 and 382 mm s⁻¹.

It is of great interest to establish if the electrolyte temperature at the pores bottom is the result of a decrease in heat removal or this is achieved by changing the diffuse and drift flows in the pore channels.

Before anodizing the temperature values were the same over the entire surface of the sample and were equal to the electrolyte temperature (Fig. 3-a). During anodizing at low stirring rate, the temperature of the sample increased to 11 °C at the left end of the sample (Fig. 3-b). If cooling is not effective at low electrolyte flows (≤ 109 mm s⁻¹), an increase in the temperature of aluminum was observed and the temperature rises extremely that led to a breakdown of the anodic layer in individual points (Fig. 4-a). When the sample was heated, vortices of the heated electrolyte were observed in the upper electrolyte layer. If the rate of stirring of the electrolyte was increased, then the temperature decreased and the process stabilized (Fig. 4-b).

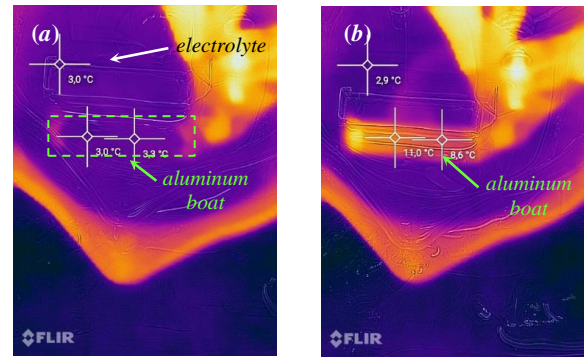


Fig. 3. Thermal image of the experimental sample before (a) and after start working mode at low stirring rate (b)

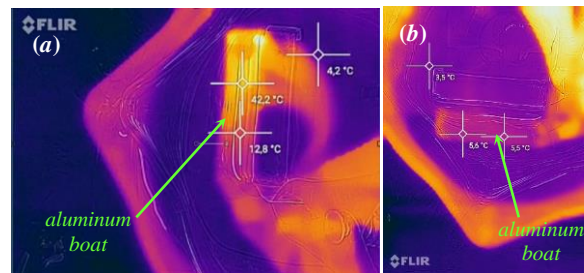


Fig. 4. Thermal image of the sample in the breakdown mode (a) and at a fast rate (b) of the electrolyte flow (flow rate 382 mm/s).

Fig. 5 shows the fluctuations of the anodizing current when the electrolyte flow rate was periodically decreased from 382 to 109 mm s⁻¹ at a stationary electrolyte temperature of 3.3 °C. It can be noted that the electrolyte temperature at the electrolyte-air interface rises slowly during anodizing process.

The change in current density and temperature of the aluminum anode with time as the electrolyte velocity decreases from 382 to 109 was studied. The experiments were carried out for oxide films with a thickness from 1 to 80 μm. The results on oxide thickness 2 and 30 μm are

presented in Fig. 6. Regardless of the oxide layer thickness and bulk electrolyte temperature, the obtained dependences of are very similar. They demonstrate that lowering the electrolyte flow rate leads to an increase in the anode temperature (T_{Al-IR}), which reflects in an increase in the anode current density, i.e. the rate of the anodizing process. In this method of stirring, the heat energy released during anodizing heats the surface layer of the electrolyte by about $0.5\text{ }^{\circ}\text{C}$ (Fig. 6, green line), while the temperature in the volume of the electrolyte (T_{E-Hg}) remains unchanged (Fig. 6-b, black lines). Therefore, the temperature most often measured and controlled by the researchers in the volume of the electrolyte does not correspond to the actual temperature of the electrolyte near the sample surface.

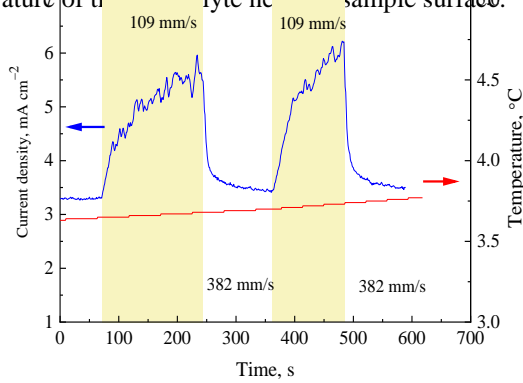


Fig. 5. Changes in anodizing current at the electrolyte flow rate 109 (shaded area) and 382 mm s^{-1} at electrolyte temperature 3.3°C

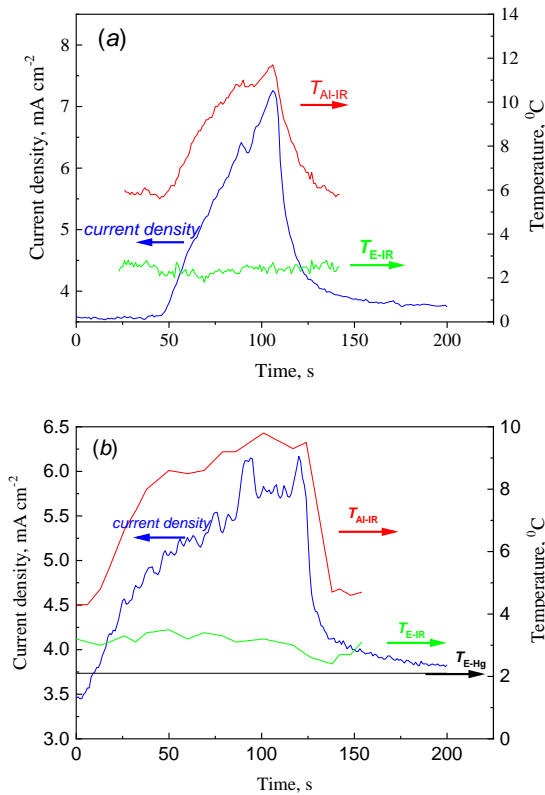


Fig. 6. Change in temperature of aluminum foil (red line) and current density (blue line) depending on the flow rate of electrolyte ranging from 382 to 109 mm s^{-1} at oxide layers with thickness of $2\text{ }\mu\text{m}$ (a) and above $30\text{ }\mu\text{m}$ (b)

In addition, at slow stirring (or at elevated anode temperature) and at thicker oxide layer, greater fluctuations in current density were observed. A similar effect of temperature on the stability of the anode current was reported in other experimental setup [5] and was associated with increased process instability at high temperatures.

The results demonstrated above refer to a short-term slow stirring within 2-3 minutes. In the case of a long process (for 40 min) at low flow rate, a linear increase in the current density was observed when the speed was increased again (Fig. 7-a, red lines). Therefore, the anode temperature rises as a result of the difficulty of removing heat from the anode surface and additional heating of the top layer of electrolyte. Such an increase in current density was not observed when the duration of electrolyte flow fluctuations was less than 2 min (Fig. 7-a, green lines). If the duration of the fluctuations is longer, then again a slight increase in current is registered with rapid stirring (Fig. 7-b, red lines).

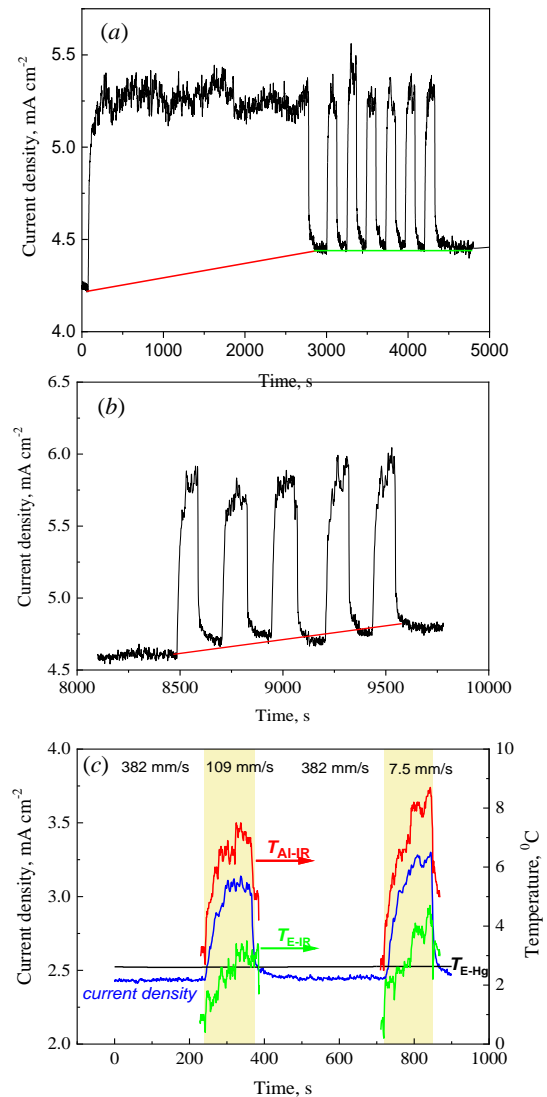


Fig. 7. Current transients for porous anodic aluminum oxide formation at a flow rate of 109 mm s^{-1} for 40 min (a) or with variation 382 to 109 mm s^{-1} with a frequency of less than 2 min (a) and more than 2 min (b); (c) flow rate changes from 382 to 109 mm s^{-1} and also from 382 to 7.5 mm s^{-1} at an electrolyte temperature of $3.3\text{ }^{\circ}\text{C}$

As noted above, slowing electrolyte rate from 382 to 109 mm s⁻¹ significantly increases the current density. However, the additional flow deceleration does not have such a noticeable effect. For example, reducing the speed from 382 to 7.5 mm s⁻¹ leads to a slight increase in the temperature of the electrolyte, and hence to a slight increase in current compared to a speed of 109 mm s⁻¹ (Fig. 7-c)

Figure 8 present SEM image of anodic aluminum oxide layer fabricated at electrolyte temperature contacting with anode T_{E-IR} of 9 °C and anode temperature about 40 °C. In this case of insufficient cooling of the sample as a result of the local temperature increase in the aluminum-oxide interface, the pore walls dissolve intensively, which leads to increase the pore diameter without changing the interpore distance.

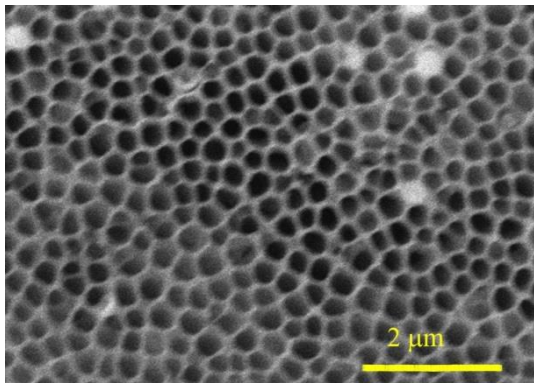


Fig. 8. Surface morphology of the porous matrix of anodic alumina with dissolved pores obtained in phosphoric acid

Using a template with wide pores, copper wires were obtained by electrochemical filling of the template at 0.3 V and then dissolving the oxide. The resulting copper wires can be used to prepare nanocomposites or introduced into pasty materials in order to change their composition and improve their properties. The copper nanowires mixed with soldering pastes to obtain a diffusion-hardening joint is presented in Fig. 9 [7].

IV. CONCLUSION

The results obtained show that by adjusting the temperature of the aluminum substrate, it is possible to maintain a higher temperature of the electrolyte at the bottom of the oxide pores and to control the process of obtaining pores with a large diameter. This makes it possible to increase the yield of copper scraping by weight per unit area of oxide. By controlling the speed of rotation of the stirrer, it is possible to rapidly cool the aluminum substrate and prevent the breakdown process. These nanowires can be used to obtain various nanocomposites.

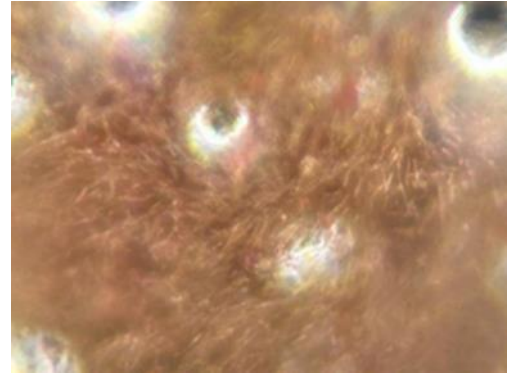


Fig. 9. Soldering paste DP 5600 (Interflux) with added nanowires.

ACKNOWLEDGMENT

This research was supported by the European Regional Development Fund within the Operational Programme “Science and Education for Smart Growth 2014-2020” under the Project CoE “National center of mechatronics and clean technologies“ BG05M2OP001-1.001-0008”.

REFERENCES

- [1] A. Ganapathi, P. Swaminathan, and L. Neelakantan, “Anodic Aluminum Oxide Template Assisted Synthesis of Copper Nanowires using a Galvanic Displacement Process for Electrochemical Denitrification”, *ACS Appl. Nano Mater.* vol. 2, pp. 5981–5988, 2019.
- [2] A. Jabbar, “Synthesis and Characterization of Noble Metal Nanowires by Electrodeposition in Porous Anodic Alumina Membranes”, *Asian J. Nanosci. Mater.*, vol 2, 120–130, 2019.
- [3] W.J. Stępniewski and M. Salerno, “Fabrication of nanowires and nanotubes by anodic alumina template-assisted electrodeposition”, *Manufacturing nanostructures*, 12, pp. 321-357, 2014.
- [4] W.J. Stępniewski and W.Z. Misiólek, “Review of fabrication methods, physical properties, and applications of nanostructured copper oxides formed via electrochemical oxidation”, *Nanomaterials*, vol. 8, p. 379, 2018.
- [5] K. Chernyakova, B. Tzaneva, I. Vrublevsky, and V. Videkov, “Effect of Aluminum Anode Temperature on Growth Rate and Structure of Nanoporous Anodic Alumina”, *J. Electrochem. Soc.*, vol. 167, 103506 (6 pp.), 2020.
- [6] K. Chernyakova, V. Videkov, B. Tzaneva, and I. Vrublevsky, “Monitoring of Electrode Temperature in Exothermic Electrochemical Process”, *IEEE XXVIII International Scientific Conference Electronics (ET2019)*, 12-14 Sept. 2019, Publisher: IEEE, DOI: 10.1109/ET.2019.8878579
- [7] V. Videkov, B. Tzaneva, Solder paste, patent pending 113111/26.03.2020