# Formation of nanoscale matrices of anodized aluminum oxide using the method of electrolyte-plasma processing of materials.

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*Abstract*

**Recently, porous anodic aluminum oxide (AAO) formed by self-organized anodic oxidation of metallic alloy A5 with 99, 75% aluminum has become one of the most popular template materials for nanofabrication. The submerged plasma glow discharge under surface of electrolyte applies to polish the surface of the aluminum foil before anodizing. As a result of a two-step process of anodizing aluminum in 2M solution of sulfuric acid at a temperature of 1 $^0$C, aluminum oxide matrices with maximum of distribution of pore diameter 20 and 84 nanometers were obtained.**

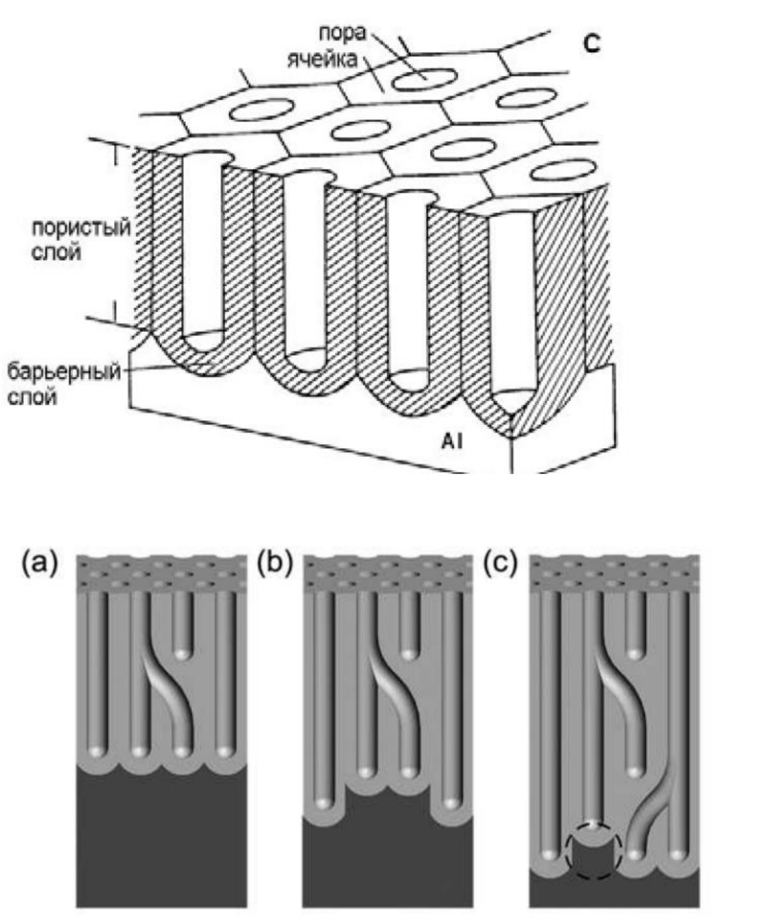



Fig. 1. Schematic illustrations structure of PAAO.

**Films of Porous Anodic Aluminum Oxide (PAAO) are probably the most widely used templates for producing highly ordered nano-fibers and arrays of nanotubes of metals, semiconductors and conductive polymers with well-defined product dimensions at a packing density of $10^9$ - $10^{11}$ 1 units/cm$^2$. It is generally recognized that the diameter and density of tubular pores located in the central part of hexagonal alumina cells can be simply controlled by changing the anodizing voltage of aluminum, while the pore length, according to the anodizing time, is regulated by tens of micrometers. In this case, the composition of the electrolyte, the electrical modes of formation, temperature, time and roughness of the sample surface have the greatest influence on the geometric parameters of the cells. The quality of the manufactured PAAO matrix and its structural perfection primarily depends on both the grade of the aluminum substrate alloy and the surface quality. Basically, foils with an Al content of 99.999% are used for the manufacture of PAAO.**
**However, recently, great interest has been shown in substrates made of alloys with a technical content of aluminum.**

**In this work, aluminum foil ФГ 0,050 x 50 Н А5 М ГОСТ 745-2014 with a thickness of 50 microns of A5 alloy with an aluminum content of 99.75% was used. The need to use a large thickness of the foil is due to the use of two stages of etching –anodizing and a significant loss of thickness for the quality of the target PAAO matrix.**
**The method of electrolyte-plasma polishing was used to polish the surface. Under the influence of voltage, a stable vapor - plasma shell appears around the sample immersed in the electrolyte and electric discharges occur throughout the treated surface. The impact of the chemical environment and electrical discharges on the surface of the part leads to cleaning and polishing of the surface of the samples. In the electrolyte-plasma technology, the processed product is an anode, and the cathode is stainless steel. High-quality polishing of aluminum and its alloys can be achieved in an electrolyte heated to 70-85°C, at a voltage of more than 250 V.**

Fig. 2. General view of the laboratory installation of electroplasma polishing.

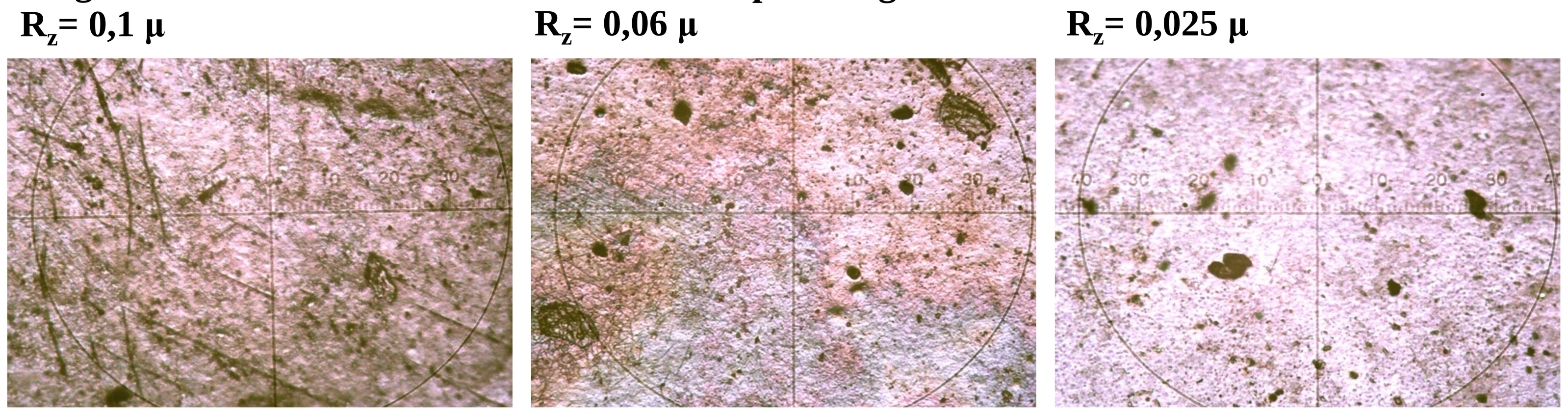
Fig. 3. The process of electrolyte-plasma polishing in 4%$FeCl_3$+2% $C_2H_2O_4$.

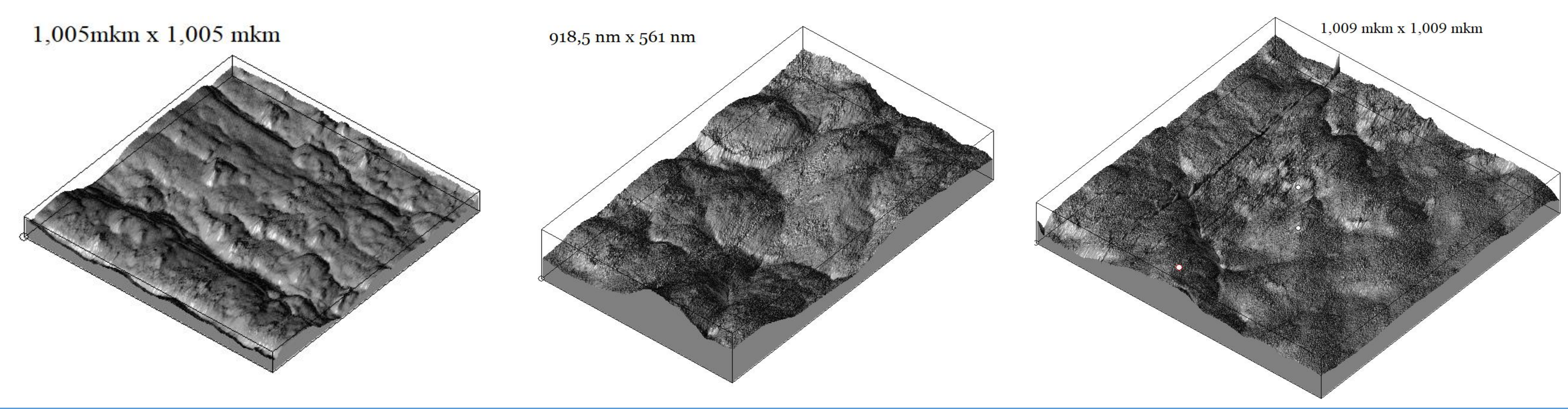
**Several different water electrolytes were used, namely 4%KCl+2%$C_2H_2O_4$, 4%$NH_4Cl$+2% $C_2H_2O_4$ and 4%$FeCl_3$+2% $C_2H_2O_4$. The following data are presented on the surface roughness of aluminum foil after electrolyte-plasma polishing in 4%KCl+2%$C_2H_2O_4$ using a Taylor Hobson Talystep mechanical profilometer and a SMM-2000-VAK scanning probe microscope.**

**Original foil** — **$R_z$= 0,1 µ**

**30 seconds of polishing** — **$R_z$= 0,06 µ**

**60 seconds of polising** — **$R_z$= 0,025 µ**




| Electrolytes | Processing time, | Voltage, | Processing temperature, | Surface appearance | Reflection coefficient | Surface roughness, |
|---|---|---|---|---|---|---|
| | s | V | °C | | %* | $R_z$, µ |
| The original foil | | | | | 60 | 2,35 |
| 4%KCl+ 2%$C_2H_2O_4$ | 30 | 280 | 85±5 | Bright | 69 | 0,1 |
| | 60 | | | | 75 | 0,06 |
| | 120 | | | | 75 | 0,025 |
| 4%$NH_4Cl$+ 2%$C_2H_2O_4$ | 30 | 290 | 90±5 | Bright | 55 | 0,55 |
| | 60 | | | | 63 | 0,37 |
| | 120 | | | | 69 | 0,32 |
| 4%$FeCl_3$+ 2%$C_2H_2O_4$ | 30 | 280 | 90±5 | Bright matte | 21 | 0,9 |
| | 60 | | | | 22 | 0,85 |
| | 120 | | | | 20 | 0,70 |

*The measurements were carried out using the device ФБ – 32

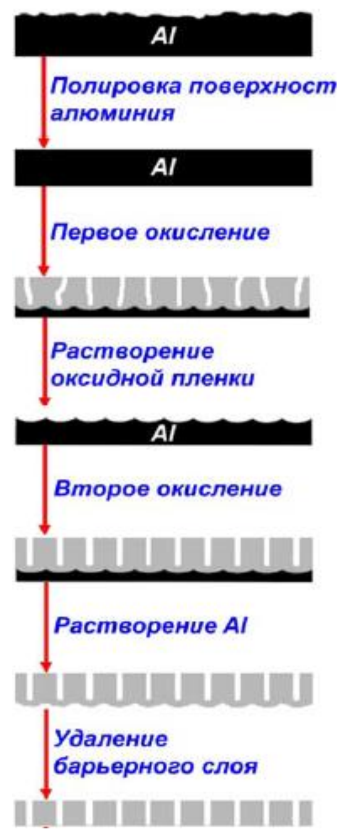



Fig. 4. The finished sample of the membrane, a transparent porous layer is highlighted in black.

**The aluminum anodizing technology represents a number of successive stages:**
**1) Preparation of the foil sample-polishing in 4%KCl+2%$C_2H_2O_4$. Processing time is 2 minutes at T = 88 ° C, voltage 280 V, current 2.25 A.**
**2) Applying a scribing film to the foil to limit the anodizing area.**
**3) Decapping of the uncoated surface in 3% HCl for 40 seconds.**
**4) The first stage of anodizing is carried out in 2M sulfuric acid for 5 minutes at a temperature of 0-1 °C.**
**5) Etching of aluminum oxide in $H_3PO_4$+$CrO_3$ at a temperature of 85 ° C for 15 minutes.**
**6) The second stage of anodizing is carried out in 2M sulfuric acid for 20 minutes at a temperature of 0-1 °C.**
**7) Removal of aluminum from the reverse side in HCl + $CuCl_2$ + $H_2O$ for 15 minutes.**
**8) Removal of the barrier layer by ion etching.**
**Below is an image from an electronic scanning microscope, which was processed using the shareware image processing program ImageJ version 1.52 a. With the help of this program, it became possible to determine the size of the pores, the degree of their roundness and their number. On the graph, you can see how the pores are distributed by size in the sample, and you can also tell about the nature of the distribution. The largest number of pores has a diameter of 20 and 84 nanometers.**
**The distribution is close to bimodal, this can be explained by recalling the mechanism of pore formation. The anodizing process is essentially divided into 2 subprocesses: etching and oxidation. At the same time, the aluminum substrate is oxidized and small seed pores are formed, they begin to expand and deepen into the oxide during the etching process. Most likely, the pores that have not had time to expand to their normal size have diameters of 20 nm. With an increase in the anodizing time and, consequently, the depth of the anodized layer, the distribution should take the form of normal.**

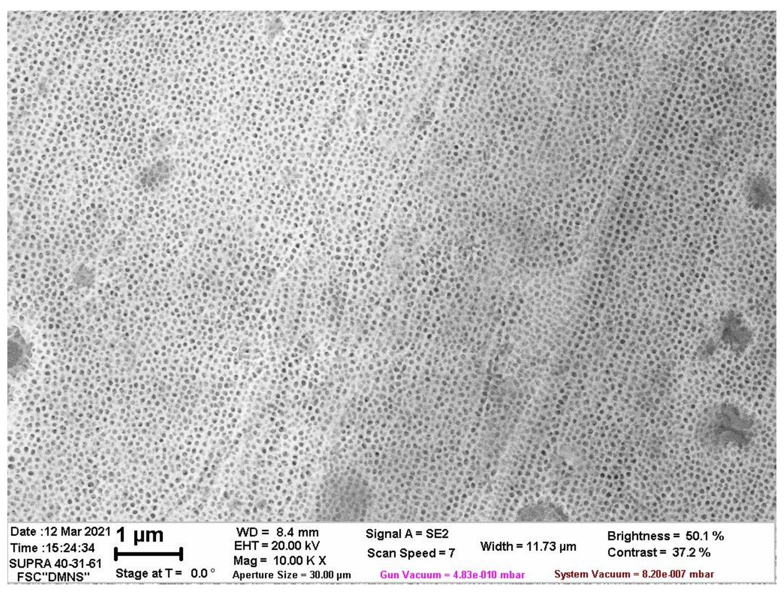



Fig. 5. SEM Image of the surface of the PAAO membrane.

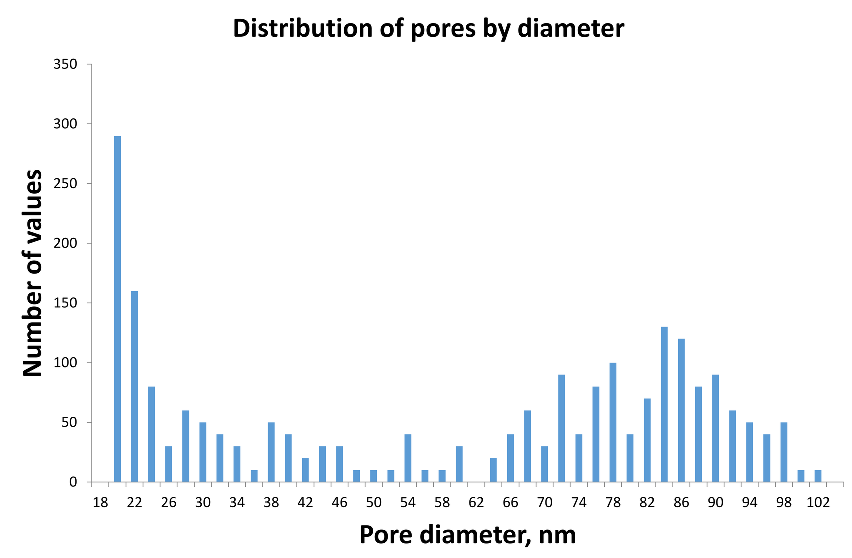



Fig. 6. Distribution of pores by diameter.

**Porous aluminum, due to its unique properties, is currently finding increasing use in such areas as:**
**- Masks for etching and spraying processes.**
**- As a matrix for filling with magnetic material for magnetic memory devices.**
**- Filter elements for cleaning liquid and gas media**
**And also:**
**- As a structural material for the manufacture of durable lightweight parts.**
**- Evaporation of liquids, including degassing of liquefied gases.**
**- Aeration of liquids to saturate them with oxygen or other gases.**
**- Damping elements on transport for damping the impact energy in collisions.**
**- As an antimicrobial coating for medicine.**

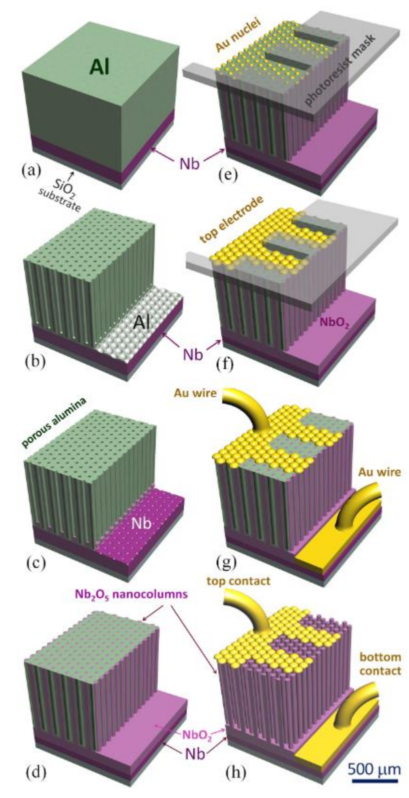


Fig. 7. PAAO as a matrix for filling with magnetic material for magnetic memory devices.

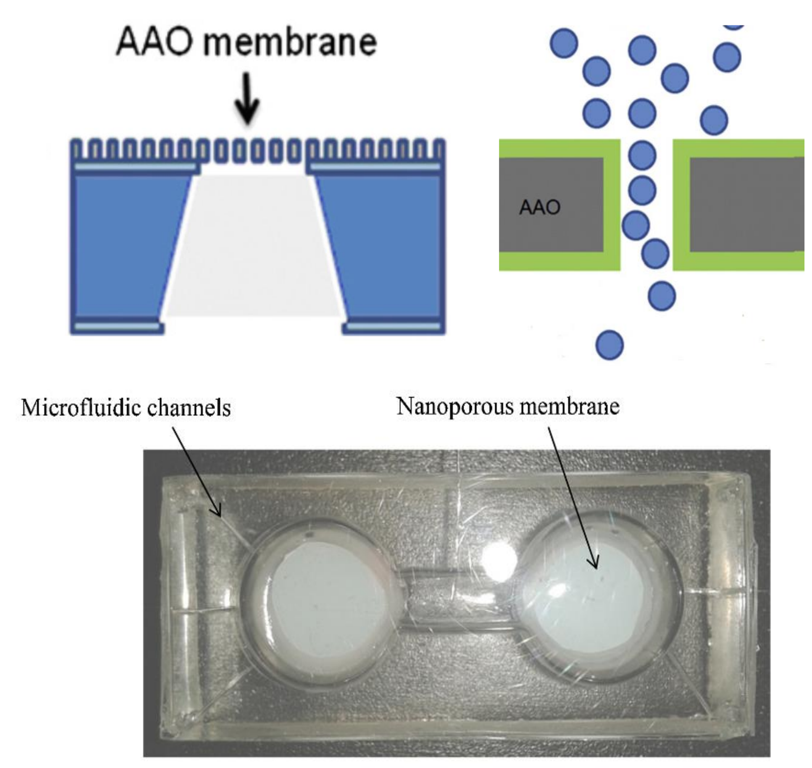



Fig. 8. PAAO as a filter element in medicine.

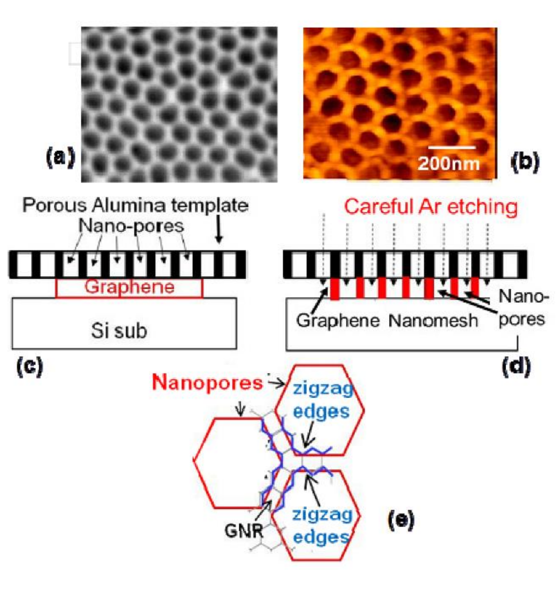



Fig. 9. PAAO as a mask.

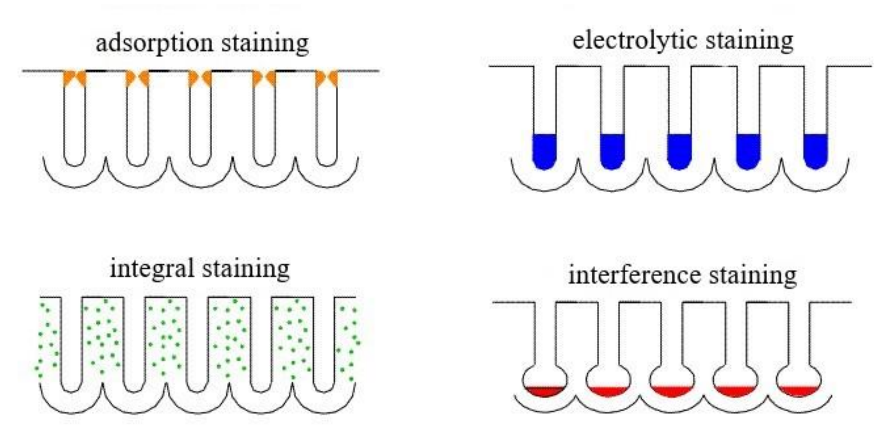



Fig. 10. PAAO for staining.

*Conclusion*

**Recently, porous anodic aluminum oxide (AOA), formed by self-organized anodic oxidation of a metal alloy A5 with 99.75% aluminum, has become one of the most popular template materials for nanotechnology. The submerged plasma glow discharge under the surface of the electrolyte is applicable for polishing the surface of aluminum foil before anodizing. As a result of a two-stage process of anodizing aluminum in 2 M sulfuric acid at a temperature of 1 $^0$C, aluminum oxide matrices with maximum pore diameter distribution of 20 and 84 nm were obtained.**