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Polishing methods for formation nanoporous anodized alumina

E.A. Grushevski ✉, N.G. Savinski, O.S. Trushin

Federal State Budgetary Institution of Science K.A. Valiev Institute of Physics and Technology of the RAS Yaroslavl Branch, Yaroslavl, Russia

✉ yaregor@mail.ru

Abstract. In the manufacture of the porous anodic aluminum oxide (PAAO) matrix, its quality and structural perfection primarily depend on both the grade of the aluminum alloy of the substrate and the quality of the surface. For the manufacture of PAAO, aluminum foil of high-purity aluminum with a content of 99.999% is mainly used. The technological scheme for obtaining highly organized porous aluminum oxide includes preliminary preparation of the foil surface of A9 alloy with an aluminum content of 99.91% by electrolytic plasma and electrochemical polishing methods in this work. Processing made it possible to obtain a surface with roughness parameters R_a = 0.008–0.038 microns. PAAO samples were obtained by double electrochemical anodizing of the prepared foil in 0.5 M oxalic acid, at a voltage of 60 V and a temperature of 25 °C and examined by scanning electron microscopy.

Keywords: aluminum, nanopores, electrolytic plasma, electropolishing

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Методы полировки для создания нанопористого оксида алюминия

Е.А. Грушевский ✉, Н.Г. Савинский, О.С. Трушин

Ярославский филиал Физико Технологического института РАН им. К.А. Валиева, г. Ярославль, Россия;

✉ yaregor@mail.ru

Аннотация. При изготовлении матрицы из пористого анодно-оксидного алюминия (ПААО) ее качество и структурное совершенство в первую очередь зависят от качества поверхности. Для получения высокоорганизованного ПААО в данной работе проведена предварительная подготовка поверхности фольги из сплава А9 с содержанием алюминия 99,91 % методами электролитно-плазменной и электрохимической полировки. Обработка позволила получить поверхность с параметрами шероховатости R_a = 0,008–0,038 мкм. Образцы ПААО получены двухстадийным электрохимическим анодированием подготовленной фольги в 0,5 М щавелевой кислоты при напряжении 60 В и температуре 25 °С и исследованы методом сканирующей электронной микроскопии.

Ключевые слова: алюминий, нанопоры, электролитическая плазма, электрополировка

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Introduction

In the last decade, there has been a revived of interest in the fabrication of a porous alumina anode layer (PAAO). The unique properties of PAAO membranes make this material a template for various nanotechnology applications. [1–4]. In this work, we used foils with an aluminum content of 99.91% and a thickness of 500 μm. Due to the imperfection of the original foil surface, it is necessary to pre-treat the surface of the foil, by electrolytic-plasma and electrochemical polishing methods.

Materials and Methods

The roughness of the foil samples was measured using a Talystep mechanical profilometer (Taylor Hobson). To assess the surface roughness, the parameter of the height of the profile irregularities was used according to the average of the absolute values of the profile deviations.

$$R_a = \frac{1}{n}\sum_{i=1}^{n}|y_i| \qquad (1)$$

where y_i are profile deviations from the baseline.

In this work, for electrolytic-plasma technology, the Al is the anode, and stainless steel is the cathode. 4% KCl + 2% $C_2H_2O_4$ was used as electrolyte. The method of electrochemical polishing was also used with $H_3PO_4 + C_3H_8O + H_2O$, $H_3PO_4 + H_2SO_4 + H_2O$, in $H_3PO_4 + CrO_3 + H_2O$ as electrolytes. Aluminum is the anode, the cathode is a platinum wire.

Results and Discussion

The quality of the fabricated PAAO matrix and its structural perfection primarily depend both on the grade of the aluminum alloy of the substrate and on the quality of the surface. Surface was polished by electrolyte-plasma and electrochemical polishing methods. If a voltage of more than 200 V is applied to the cathode and anode electrodes located in an aqueous electrolyte solution, then the current density quickly reaches 30 A/cm^2, which causes instantaneous evaporation of water, the formation of a vapor-gas shell and the formation of a plasma discharge. High-quality polishing of aluminum and its alloys can be achieved in an electrolyte heated to 70–85 °C at a voltage > 250 V [5]. The most widely used method of electrochemical methods of material processing is electro polishing, which combines high-quality polishing with obtaining a shiny surface. In this work, aluminum was polished while maintaining a current density of 25 A/dm^2 for 5, 10, 15, 20 minutes in $H_3PO_4 + C_3H_8O + H_2O$, $H_3PO_4 + H_2SO_4 + H_2O$, in $H_3PO_4 + CrO_3 + H_2O$. All data was shown in Table.

Table

Roughness data for electrolyte-plasma and electrochemical technologies

N	R_a, μm	Sample
1	0.67	original foil
2	0.016	foil polished in $H_3PO_4 + H_2SO_4 + H_2O$
3	0.012	foil polished in electrolytic plasma in 4% KCl + 2% $C_2H_2O_4$
4	0.008	foil polished in $H_3PO_4 + C_3H_8O + H_2O$
5	0.038	foil polished in $H_3PO_4 + CrO_3 + H_2O$

The method of electrolytic-plasma polishing is slightly inferior to the method of electrochemical polishing in the quality of the surface obtained, but the processing time is significantly lower. The durations of the processes are from 30 to 120 seconds and from 5 to 20 minutes for electrolytic-plasma and for electrochemical technologies, respectively. The method used for electrochemical anodizing of the prepared foil is a classic version of two-stage anodizing in 0,5 M oxalic acid, at a voltage of 60 V and a temperature of 25 °C [6]. In order to control the effect of preprocessing on the quality of the obtained matrices, we examined PAAO chips by scanning electron microscopy. Initially, the quality of the Al substrate, its surface structure and/or any surface pre-treatments will have a significant effect on the morphology formed on the surface of the substrate during the anodizing process. Surface treatments prior to anodizing can have a significant effect on the self-ordering of pore structures formed on the substrate surface during anodizing. This is because the pore nucleation mechanism is a combination of both random nucleation and nucleation caused by exposure to surface defects such as scratches, pits, impurities, and grain boundaries. Fig. 1, *a* shows areas with different directions of net growth. The polishing process eliminates surface defects and minimizes the possibility of pores crossing as it was shown in Fig. 1, *b*.

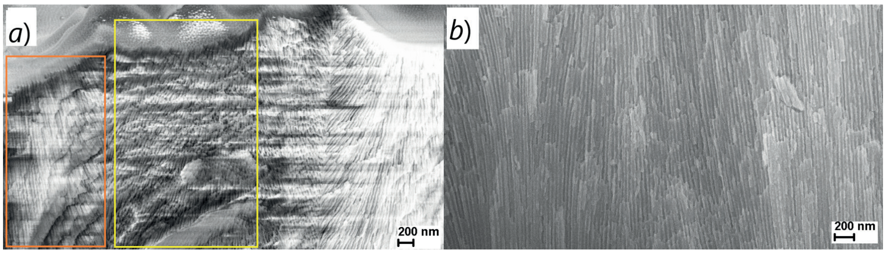

Fig. 1. SEM image of PAAO without pre-polishing (*a*) and with pretreatment (*b*)

Fig. 2, *a* shows the SEM image of the PAAO matrix without pretreatment. There are the peaks of irregularities around which the ordering of the pores is disturbed. After processing, surface defects are small and have little effect on pore formation. The pore diameter distributions maximums are at 95 nm and 80 nm, for an unpolished and a polished substrate, respectively.

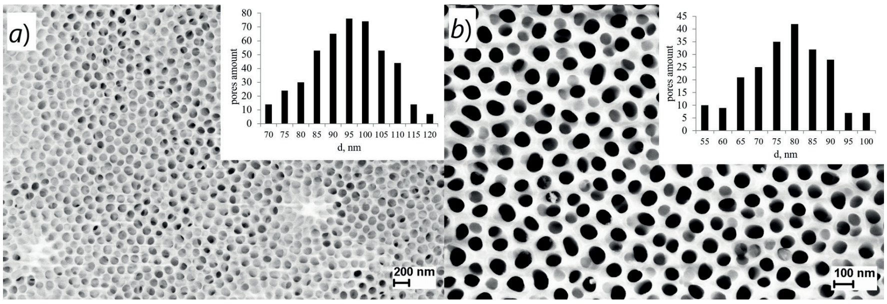

Fig. 2. SEM image of PAAO without pre-polishing (*a*) and with pretreatment (*b*) and pores distribution

Conclusion

A technological scheme for obtaining highly organized porous aluminum oxide has been developed, including preliminary preparation of the surface of aluminum foil using a method of submerged plasma glow discharge under the surface of the electrolyte, as well as an electrochemical method. PAAO samples were obtained by double electrochemical anodizing of the prepared material in 0.5 M oxalic acid, at a voltage of 60 V and a temperature of 25 °C and were investigated by scanning electron microscopy.

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THE AUTHORS

GRUSHEVSKI Egor A.
yaregor@mail.ru
ORCID: 0000-0003-2267-4260

TRUSHIN Oleg S.
otrushin@gmail.com
ORCID: 0000-0000-0000-0000

SAVINSKI Nikolay G.
savinski1@yandex.ru
ORCID: 0000-0003-1913-0924

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