New approach of electrochemical formation of nanostructured Al_2O_3 membranes

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INTRODUCTION

This paper discusses the method for producing alumina membranes [1] by the two-step two-side anodization to a complete end-to-end oxidation of initial aluminum foils. The main problem with this approach is associated with the need to ensure high surface quality of the initial Al substrates. The surface roughness causes the effect of the supply potential cutoff at the final stage of the two-side anodization resulting in the local not anodized Al inclusions inside the Al_2O_3 membranes at the interface of junction of the two opposing barrier layers. These Al inclusions are eliminated by bipolar anodizing after the deep end-to-end anodization.

EXPERIMENTAL STUDY

The 60, 110, and 160 μm thick aluminum foils with a high purity (99.99 %) were used as initial material. After repeated rolling using polished platens, foils were subjected to the thermo-straightening under the pressure of ~10^7 Pa at 350 °C for 1 h to relieve mechanical stress and increase the plasticity parameters. Then the samples 60×48 mm in size were formed by stamping. The samples were chemically cleaned in CrO_3:H_2SO_4 (1:100) for 2-3 min. To smooth and eliminate the microroughness, the electrochemical polishing of aluminum were carried out in the electrolyte based on perchloric and acetic acids (22 % : 78 %). Thereafter the thickness of the Al plates was ~50, 100, 150 μm. The two-side anodization was made in two steps in the 7 % electrolyte of $H_2C_2O_4$ at constant voltage of ~55 V. The first anodization step was performed for 10 min resulting in the formation of hexagonally close-packed arrays at the interface between the porous alumina layer and the aluminum substrate. Then, the porous alumina film formed is selectively dissolved in the CrO_3:H_3PO_4:H_2O solution at 85 ^oC for 5 min. Patterns that are replicas of the hexagonal pore array are preserved on the fresh aluminum surface. This allows the preparation of pores with a high regularity by a subsequent second anodization under the same conditions as the first anodization. The deep two-side end-to-end porous anodization was performed until the fall of current in the electrochemical bath to almost zero when the two oxide layers growing towards each other are connected.

RESULTS AND DISCUSSION

The two-side two-step anodization of aluminum foils resulted in the formation of nanostructured membranes 73, 145, and 216 μm in thickness. The membranes consisted of two-layer nanoporous alumina with pores ~55 nm in diameter symmetrically located on two sides of the membranes (fig. 1). The total thickness of the barrier layers was ~ 140 nm. The volume growth coefficient in the conversion of Al to Al_2O_3 was 1.44-1.46.

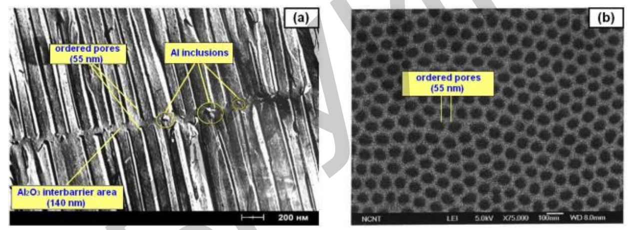

Fig. 1 SEM images of alumina membrane obtained by the two-side two-step anodization: cross-section (a) and top view (b)

The basic idea of the bipolar anodization is to use a two-chamber electrolytic bath, in which the alumina membrane with Al inclusions was placed as an insulating partition. One of the chamber is filled with the anodization electrolyte (7 % $H_2C_2O_4$), while the buffer electrolyte (10 % $CuSO_4$) is used in the second chamber. The cathode electrode (-) is placed in the first chamber and the anode electrode (+) is connected to the second one. When the current was switched on (U ~55 V), a positive charge appeared on one side of the membrane opposite the Al inclusions. The membrane became an anode, and anodic oxidation (anodizing) of Al inclusions took place. The second side of the membrane was charged negatively, became a cathode. The recovery of buffer electrolyte cations (Cu^{2+}) on the cathode side opposite the Al inclusions was observed with a guaranteed absence of sparks and burn-through of the oxidized layer in these zones.

CONCLUSION

Thus, the two-step two-side anodization of aluminum foils followed by the bipolar anodization and further etching allows nanostructured alumina membranes to be formed. Highly ordered nanostructured nature of their cellular porous morphology that can be controlled by electrochemical and temperature modes of the electrochemical anodizing process appears to have considerable promise.

REFERENCES

1. Sokol V.A., et.al Doklady BGUIR: Application features of porous alumina 2 (2012).