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Properties of nanostructures obtained by anodization of aluminum in phosphoric acid at moderate potentials

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Abstract. The influence of the process duration, anodizing potential and methanol addition on the structural features of porous anodic alumina formed in a 0.3 M H₃PO₄ solutions by two-step self-organized anodizing was investigated for potentials ranging from 100 to 170 V. The structural features of porous structures including pore diameter and interpore distance were evaluated from FE-SEM top-view images for samples anodized in the presence and absence of methanol. For the highest studied anodizing time and methanol volume fraction, an excellent agreement between experimental values of the interpore distance and theoretical predictions was observed. The pore arrangement regularity was analyzed for various electrolyte compositions and anodizing potentials. It was found that the regularity ratio of porous alumina increases linearly with increasing anodizing potential and time. The addition of methanol improves the quality of nanostructures and especially better uniformity of pore sizes is observed in the presence of the highest studied methanol content.

1. Introduction

Anodization of aluminum has become one of the most popular processing ways used for formation of porous structures with a pore diameter ranging from about 10 to over 300 nm [1-3]. The anodization of aluminum that leads to a porous structure is usually performed in electrolytes containing sulfuric, oxalic or phosphoric acid [1]. The structural features of porous alumina films such as: pore diameters, interpore distance and porosity strongly depend on the chosen electrolyte and anodizing potential [1].

Porous alumina membranes (AAO) are widely used for fabrication of various nanostructures and nanodevices. Over the last decade, many materials including nanowires, nanotubes and nanodot arrays have been fabricated by deposition of various metals, semiconductors, oxides and polymers inside the pores of AAO membranes [4].

It is widely recognized that anodization of aluminum in phosphoric acid results in nanoporous structures but, the best pore arrangement is obtained only at anodizing potentials very close to 195 - 200 V [1]. Frequently, rising potential above 160 V causes burning of the oxide layer and promotes active dissolution of aluminum instead of anodic growth of porous oxide.

The aim of this work was to investigate the influence of anodizing conditions on the structural features of self-organized porous anodic alumina formed in H₃PO₄ by two-step anodizing at potentials between 100 and 160 V and optimization of those conditions for fabricating of high-ordered

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nanoporous structures.

2. Experimental

High-purity (99.9995 %, Alfa Aesar) annealed Al foil, was used as a substrate for anodization. Prior to anodizing samples were decreased in ethanol and electropolished in a mixture of HClO_4 and $\text{C}_2\text{H}_5\text{OH}$ (1:4 vol.) at constant current density of 500 mA cm^{-2} at 10°C for 1 min. A two-step anodization procedure was employed to obtain porous alumina structures. In the two-step anodization procedure, an alumina layer formed during the first anodization was chemically removed and then the second anodization was performed under the same conditions as were used in the first step. After the first step of anodization the oxide layer was chemically removed in a mixture of 1.8 wt.% H_2CrO_4 and 6 wt.% H_3PO_4 at 60°C for 120 min.

A working surface area of Al anode was 0.5 cm^2 . A Pt grid was used as a cathode, and a distance between both electrodes was about 3 cm. The electrolyte was continuously stirred (300 rpm) during anodizations. The surface morphology of alumina layer was investigated using a field emission scanning electron microscope (Hitachi S-4700). The scanning probe image processor WSxM 4.0 Develop 7.6 [5] was employed to calculate and analyze two-dimensional fast Fourier transforms (2D FFT) of FE-SEM images and the ImageJ 1.37v [6] software was used for estimation of values of pore diameter.

3. Results and discussion

3.1. The effect of anodizing potential

The regularity of nanopore arrangement and structural features of porous anodic alumina was investigated for samples anodized at different cell potentials ranging from 100 to 160 V. Two-step anodizing of aluminum was carried out in a 0.3 M H_3PO_4 aqueous solution or a methanol-water mixture (1:4 vol.) at the temperature of 0 and -5°C . Typical FE-SEM top-views of porous structures with FFT images and intensity profiles of FFT images for samples anodized in 0.3 M H_3PO_4 at the lowest (100 V) and highest (160 V) anodizing potentials are shown in figures 1A and 1B, respectively.

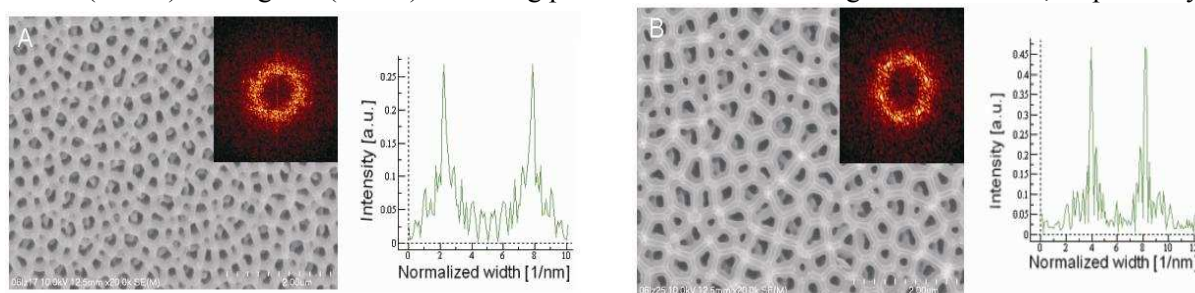


Figure 1. SEM top-view micrographs with FFT images and FFT intensity profiles for samples anodized at 100 V (A) and 160 V (B). The anodization was carried out in 0.3 M H_3PO_4 at 0°C . The duration of the first and the second step was 14 h.

A random arrangement of pores and lack of uniformity in the pore diameter and pore shape were observed for all studied anodizing potentials. This fact is qualitatively confirmed by wide ring-shapes observed in FFT images (figure 1).

In order to get a deeper insight into the regularity of pore arrangement, a regularity ratio (R_i), defined as a ratio of the maximum intensity of the peak in the FFT profile to the width of the peak at half-maximum divided by the square of the interpore distance, was calculated from FFT profiles for various anodizing potentials. The dependence between an average regularity ratio and anodizing potential is shown in figure 2A for anodizing carried out in water and methanol-water systems.

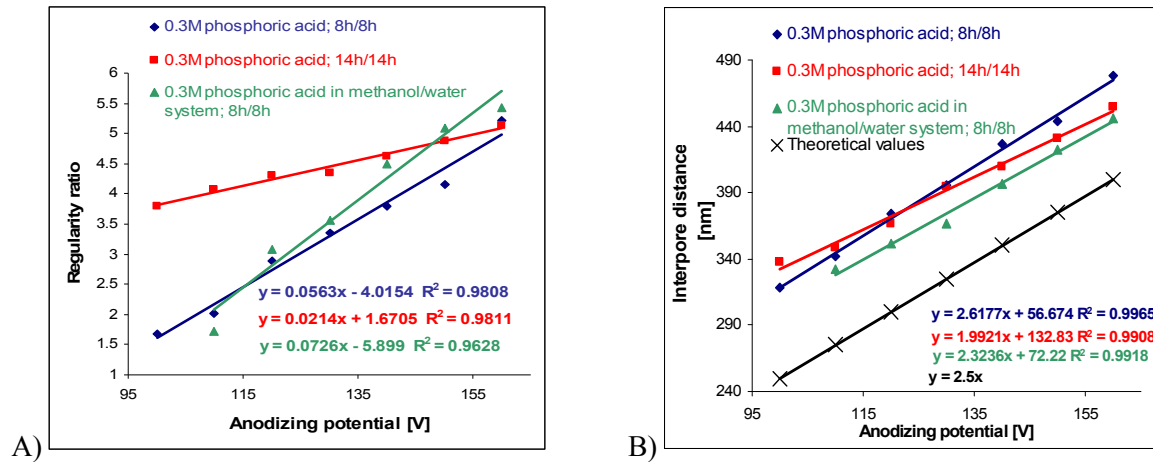


Figure 2. The effect of anodizing potential on the regularity ratio (A) and interpore distance (B) of the nanostructure formed in 0.3 M H₃PO₄. Anodization was carried out at 0 °C for samples anodized without methanol and at -5 °C with a methanol addition.

It is generally accepted that interpore distance (D_c) in porous anodic alumina increases linearly with increasing anodizing potential (U) according to the following equation:

$$D_c = \lambda_c \cdot U \quad (1)$$

where λ_c is a proportionality constant equals to about 2.5 nm V⁻¹. An average interpore distance of the nanostructure can be easily calculated from the radius of the FFT pattern. The average interpore distance calculated for all examined samples and theoretical values predicted from equation (1) are shown in figure 2B. A strong linear relationship between interpore distance and anodizing potential was observed independently of the electrolyte composition and duration of the process. For samples anodized in the methanol-water system, better consistency with the theoretical value is observed. The average proportionality constants for examined samples are collected in table 1.

Table 1. The proportionality constant between interpore distance and anodizing potential for various durations of both anodizing steps.

Duration of both anodizing steps [h]	Temperature [°C]	Electrolyte	Proportionality constant λ_i (nm V ⁻¹)
8	0	0.3 M H ₃ PO ₄	3.1 ± 0.1
14	0	0.3 M H ₃ PO ₄	3.0 ± 0.2
8	-5	0.3 M H ₃ PO ₄ in methanol-water mixture (1:4 vol.)	2.8 ± 0.1
Theoretical value			2.5

Once again, an excellent agreement between the experimental proportionality constant and theoretical value is observed for samples anodized in a methanol-water mixture (1:4 vol.). This results suggests that anodization of aluminum performed in a methanol-water system could lead to porous structures with a better regularity of pore arrangement.

Due to the fact that porous anodic alumina films obtained by anodizing of aluminum in phosphoric acid exhibited the complex structure with subpores formed underneath on the surface (clearly visible in figure 1), the average pore diameter was not estimated and the analysis of potential influence on pore diameter was not performed.

3.2. The effect of anodizing time

The effect of the anodization duration on the arrangement of pores and structural features of porous anodic alumina films formed in 0.3 M H₃PO₄ at 160 V and 0 °C was investigated in details. Typical

FE-SEM top-view micrographs with FFT images and FFT intensity profiles are shown in figure 3 for various anodizing times ranging from 8 to 40 h.

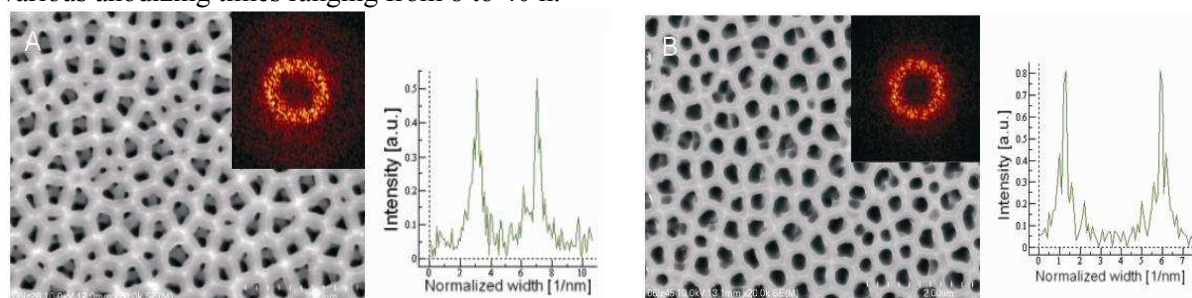


Figure 3. FE-SEM top-view micrographs with FFT images and intensity profiles of FFT images for samples anodized in 0.3 M H_3PO_4 at 160 V and 0 °C. The duration of the first and second anodizing step was 8 h (A) and 40 h (B).

However, the qualitative analysis of the pore arrangement performed on the basis of FFT images, does not give a clear answer about the effect. The quantitative inspection, exploiting the calculated average values of regularity ratio (table 2), shows that increasing duration of both anodizing steps improves the regularity of pore arrangement and uniformity of pore-shapes.

Table 2. The anodizing time influence on the average regularity ratio (R_i) for samples anodized in 0.3 M H_3PO_4 at 160 V and 0 °C.

Duration of both anodizing steps [h]	8	14	20	40
R_i [a.u.]	5.21	5.14	7.84	9.61

This can be attributed to the fact that in the two-step self-organized anodization of aluminum a significant extension of the first anodizing step improves considerably the regularity of array of nano-periodic concave, consisting of a triangular lattice structure, on the aluminum substrate after the oxide layer removal. The periodic concave triangular features formed on the aluminum surface serve as nucleation sites for the formation of pores during the second anodizing step. In consequence, the regularity of pore arrangement observed after the second anodization is highly improved.

On the other hand, is clearly visible from figure 3 that increasing anodizing duration increases the size of pores. The average pore diameter estimated from FE-SEM top-views for various anodizing durations is shown in figure 4A. With increasing anodizing time the pore diameter rises gradually and for the longest duration is similar to the theoretical value. This increase in the pore diameter could be a result of prolonged etching of alumina in the acidic electrolyte used for anodizing. In addition, the complex network of pores containing subpores disappears due to the electrolyte etching action. The change of interpore distance as a function of anodizing time is shown in figure 4B. Surprisingly to expectations, a slight decrease of interpore distance towards the theoretical value is observed with an extension of anodizing duration. This is caused by increasing structural regularity of pore arrangement with increasing anodizing time. A gradual improvement of the pore lattice regularity towards the perfect hexagonal arrangement is observed with the increasing anodizing duration.

It is worth noting that with a significant extension of the anodizing time a considerable improvement of pore arrangement have not been observed. Therefore, from an economical point of view potentiostatic anodizing of aluminum in H_3PO_4 in the range of potential between 100 and 160 V, even in the presence of methanol, does not give satisfying results and another approaches to structure regularity improvement have to be considered.

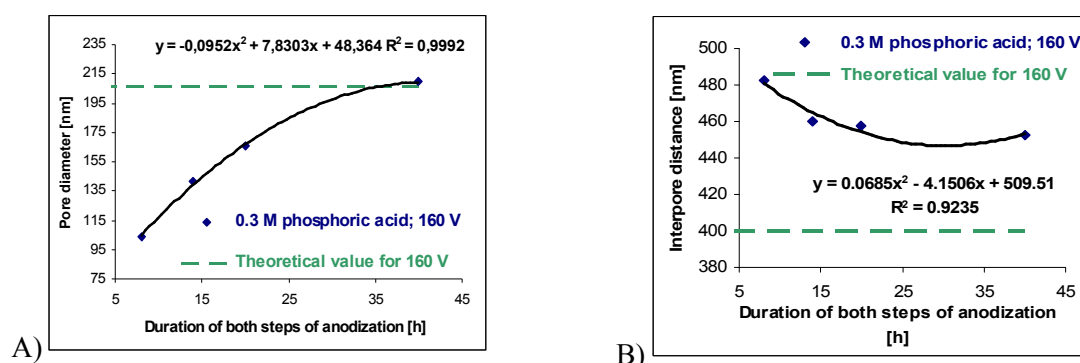


Figure 4. The effect of the duration of both anodizing steps on the average pore diameter (A) and interpore distance (B) of anodic porous alumina formed in 0.3 M H₃PO₄ at 160 V and 0 °C.

3.3. The effect of methanol addition

The influence of methanol addition on regularity of the pore arrangement and structural features of porous anodic alumina was studied for the anodizing potential of 160 V at -5 °C. The presence of methanol in the electrolyte allows to decrease the anodizing temperature to -5 °C. For all studied methanol additions, the duration of both anodizing steps was 8 h. Figure 5 shows typical FE-SEM top-views with FFT images and intensity profiles for samples anodized in a methanol-water mixture 1:4 vol. (figures 5A and 5C) and 1:1 vol. (figure 5B) containing 0.3 M H₃PO₄.

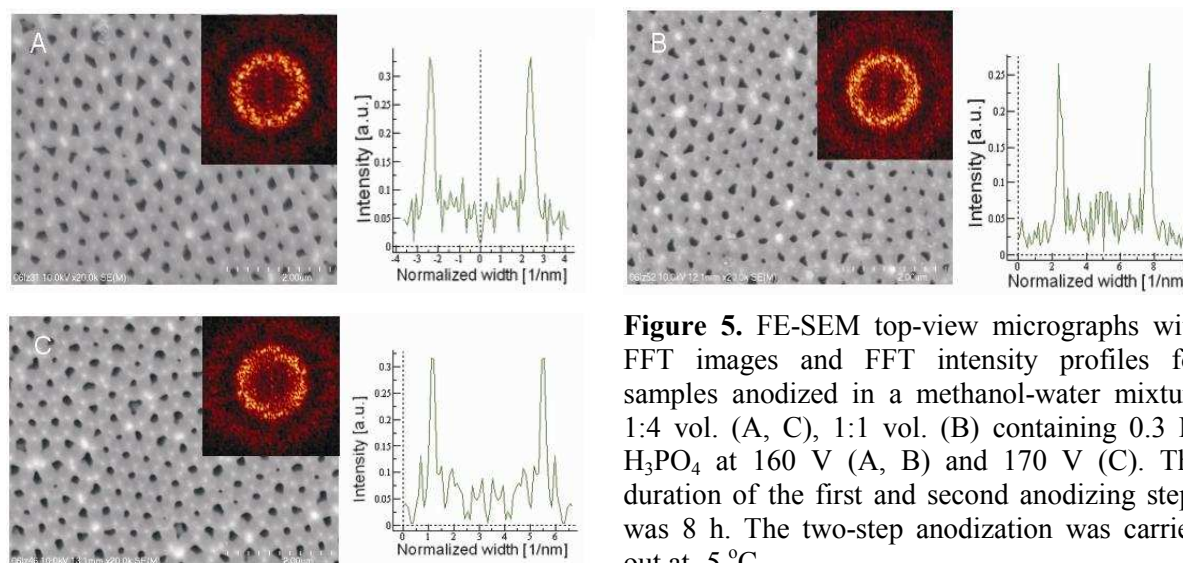


Figure 5. FE-SEM top-view micrographs with FFT images and FFT intensity profiles for samples anodized in a methanol-water mixture 1:4 vol. (A, C), 1:1 vol. (B) containing 0.3 M H₃PO₄ at 160 V (A, B) and 170 V (C). The duration of the first and second anodizing steps was 8 h. The two-step anodization was carried out at -5 °C.

For the methanol-water system (1:4 vol.), the range of applicable potential window broadens and a maximum anodizing potential that could be applied without causing a serious burning phenomena is 170 V (figure 5C). It can be attributed to the evaporative cooling effect of methanol at the pore bottoms. It should be noticed that during the anodization temperature at the pore bottoms increases due to the Joule heating effect. Methanol, as a solvent with a lower evaporating temperature than water decreases the temperature at the pore bottoms more effectively. With increasing methanol content and increasing anodizing potential regularity in the pore arrangement increases gradually (figure 5). Some hexagonally arranged cells are clearly visible in the FE-SEM images. Contrary to anodization carried out in the absence of methanol (figures 1 and 3), the complex pore structure with subpores disappears.

The quantitative investigation of the pore arrangement, based on the analysis of intensity profiles revealed that the average regularity ratio increases with increasing methanol fraction (table 3).

Table 3. The effect of methanol volume fraction on regularity ratio (R_i) for samples anodized in a methanol-water mixture containing 0.3 M H_3PO_4 at 160 V. The anodizing temperature was -5°C and the duration of both anodizing steps was 8 h.

Volume fraction of methanol	0	0.2	0.33	0.5
R_i [a.u]	5.21	5.42	7.55	7.77

The presence of methanol in the anodizing electrolyte influences the structural features of porous anodic alumina. Figure 6 shows dependence of the volume fraction of methanol in the electrolyte on the average interpore distance for samples anodized at 160 V. A linear decrease in the interpore distance is observed with the increasing methanol content. For the highest methanol content, the observed average interpore distance is consistent with a theoretical value predicted from equation (1).

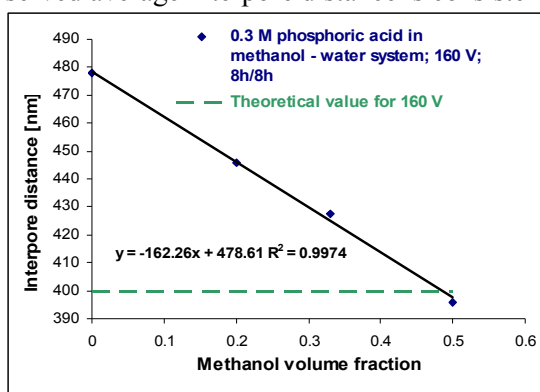


Figure 6. The effect of methanol addition on the average interpore distance of nanostructures formed in 0.3 M H_3PO_4 at 160 V and -5°C . The duration of both anodizing steps was 8 h..

Further studies are required to establish the optimal methanol addition in the typical temperature used for anodizing in phosphoric acid (0°C). Moreover, our attention is also focused on identifying the effect of different solvent additions with low boiling points on the structural features of AAO and the regularity of porous structure.

Conclusions

In summary, increasing anodizing potential and process duration as well as an increasing methanol content in the electrolyte used for anodization improve considerably the arrangement of pores in AAO. An excellent consistency between experimental results and theoretical predictions of the interpore distance was observed for the highest studied anodizing time and the highest methanol content in the anodizing electrolyte.

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