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STUDY OF MICROSTRUCTURE OF POROUS ANODIC ALUMINA FILMS FORMED IN MALONIC ACID IN THE WIDE RANGE OF ALUMINUM ANODIZING VOLTAGES

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Abstract: In present paper the microstructure parameters of porous anodic alumina films formed by the anodizing of aluminum in the aqueous solution of malonic acid at different anodizing voltages was studied. The morphology of structured surface of aluminum film was studied using a scanning electron microscope after selective removal of anodic film. The results obtained for anodic films formed in malonic acid during anodizing in the range of 15-80 V allowed to determine that change in the interpore distance with the anodizing voltage is linear function with a slope of 1.45. The key conclusion was made that mechanical stress in anodic alumina layer is the main factor responsible for formation of the nanoporous structure of anodic alumina films.

Keywords: porous anodic alumina, nanostructured aluminum surface, interpore distance, malonic acid, mechanical stress

1. Introduction

The structure of porous anodic alumina films is a system of ordered cells having a pore in the center. The ability to control the parameters of the porous microstructure of anodic alumina using anodizing modes allows using such anodic films as nanofibers, carriers for catalysis and membranes for the synthesis of various functional nanomaterials [1-4].

It is well known that for porous anodic alumina films fabricated using mild anodization (MA) the interpore distance (D_{inter}) linearly increases with the anodizing voltage (U) [2,5]. In case of the most commonly used electrolyte systems, such as sulfuric, oxalic, phosphoric and citric acids, the slope of the D_{inter}-U curve is close to 2.5 nm V^{-1} [6]. Recently, however, in the studies of porous anodic alumina growth formed in oxalic acid, it was found that such linear relationship at low anodizing voltages has a much smaller slope than it could have been expected. At voltages of up to 30 V, the slope of the D_{inter}-U curve was 1.45 nm V^{-1}, then, when the voltage reached 40 V, the slope switched to 2.5 nm V^{-1} [7]. The results obtained clearly show the need for more detailed studies of the initial region of the D_{inter}-U curve in other electrolytes of aluminum anodizing.

In this study, malonic acid was selected as the electrolyte, because it is used for fabrication of porous anodic alumina films, but data on anodic oxide growth is not enough [8-10]. According to [6], for porous anodic alumina films formed in malonic acid at 120 V, D_{inter} was 300 nm and the slope between D_{inter} and U was found to be 2.5 nm V^{-1}. At the same time, in the literature, there is no data on the character of the dependence of D_{inter} on U for anodizing voltages less than 100 V in malonic acid.

The aim of the paper was to study the microstructure parameters of porous anodic alumina films formed by anodizing of aluminum in the aqueous solution of malonic acid at different anodizing voltages.

2. Experimental

Anodic alumina films were formed on the aluminum foil 25.0 µm thick (99.9 % purity, Alfa Aesar). Anodizing of the specimens of aluminum foil was carried out in the double-electrode temperature-controlled 3L cell with the platinum grid cathode. A 0.8 M solution of malonic acid ($HOOCCH_2COOH$) was used as the electrolyte for porous anodic alumina formation at (20 ± 0.5) ºC. The electrochemical power supply was potentiostat/galvanostat P5827M. Porous alumina films were grown under controlled potential conditions for 10 min. The specimens were carefully rinsed in a distilled water after anodizing.

The microstructure of porous anodic alumina films formed in the 0.8 M solution of malonic acid was investigated by the imprints of cells on aluminum surface. The morphology of the structured surface of aluminum film was studied using scanning electron microscope (ESCALAB MK II) after the selective removal of the anodic film by immersion in a hot solution (80 ºC) of 0.4 M H_3PO_4 and 0.2 M CrO3 for 2 min.

3. Results and discussion

The SEM image of nanostructured aluminum surface after the selective removal of porous anodic alumina film formed in malonic acid at 80 V is demonstrated in Figure 1.

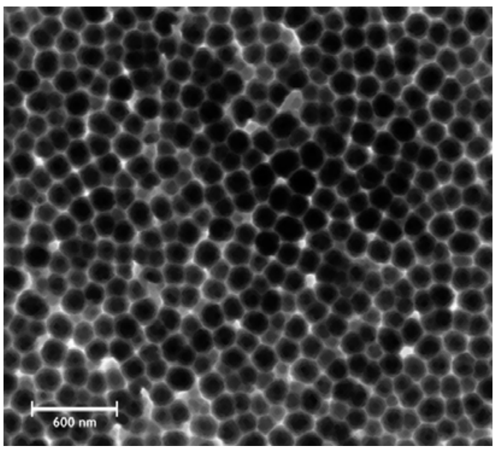

Figure 1. SEM image of the structured aluminum surface after selective removal of porous anodic alumina film formed in malonic acid at 80 V.

The dimples on the surface of aluminum, formed at the places of contact of the barrier oxide layer of each pore with aluminum, indicate the locations of cells of porous anodic alumina. The distance between the centers of adjacent dimples on the aluminum surface coincides with the interpore distance for porous alumina. The distribution of distance between the centers of adjacent dimples (interpore distance for porous alumina) was calculated by the ImageJ software.

For that, first, the dimple centers were determined by ImageJ. Then, for each center, the area was gradually increased by segmentation method until the segments formed were in contact with each other from different sides. As a result, a computer model of the cellular structure of porous alumina surface was obtained based on the nanostructured aluminum surface (Figure 2).

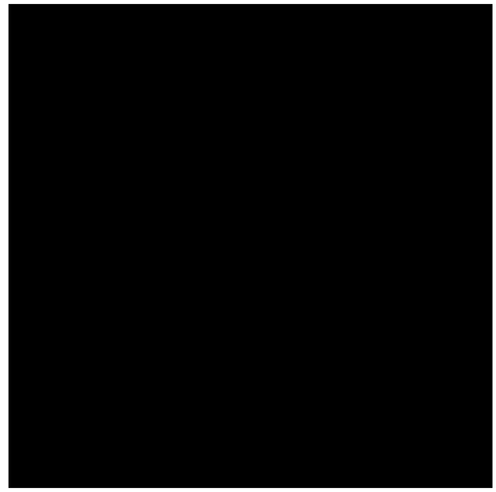

Figure 2. Computer model of the cellular structure of porous anodic alumina surface (malonic acid, 80 V) obtained by ImageJ.

The computer model made it possible to find the distribution of interpore distance for each anodizing voltage in malonic acid. Then, the experimental distribution of interpore distance was approximated using the Gauss model. The peak in the Gauss fitting curve corresponded to the main interpore distance for the porous alumina film. Figure 3 demonstrates the distribution of interpore distance with Gauss fitting for SEM image of nanostructured aluminum surface after removal of porous anodic alumina film (80 V) (Figure 1).

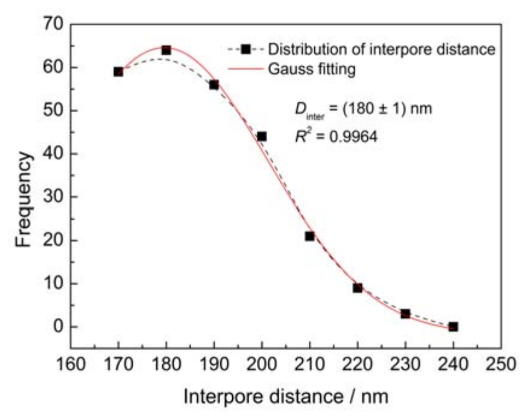

Figure 3. The distribution of interpore distance calculated by ImageJ (black) and Gauss fitting (red) for porous anodic alumina film formed in malonic acid at 80 V.

As can be seen from Figure 3, the porous anodic film obtained at 80 V had interpore distance of 180.0 ± 1.0 nm. Similarly, for each anodizing voltage, interpore distance was calculated using a Gaussian model. The resulting dependence of interpore distance on the anodizing voltage (voltage range from 15 to 80 V) is presented in Figure 4.

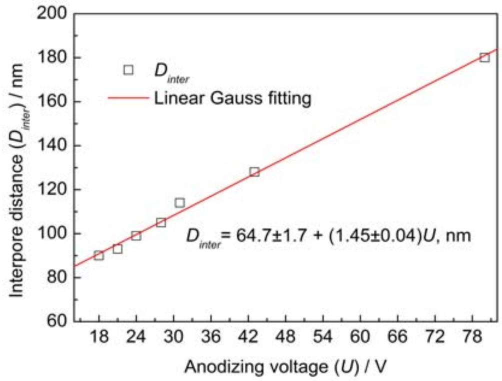

Figure 4. Evolution of the interpore distance (D_{inter}) as a function of anodizing voltage for porous anodic alumina films formed in malonic acid.

As can be seen from Figure 4, the D_{inter} -U curve is a linear function with a slope of 1.45. Noteworthy, that for anodic films formed in malonic acid at 120 V, the slope of the D_{inter}-U curve is higher and equals to 2.5 nm V^{-1} [6]. The result obtained in malonic acid fully coincides with features of the slope at two regions of the D_{inter}-U curve in oxalic acid. The slope in the first (initial) region was 1.45 nm V^{-1} and then, when a certain voltage was reached, the slope changed to 2.5 nm V^{-1} (the second region). Moreover, the nature of change in the proportionality factor D_{inter}/U vs. U in case of malonic acid (exponential decay) (Figure 5) coincided with characteristics of this coefficient at the initial region of the curve in oxalic acid [11].

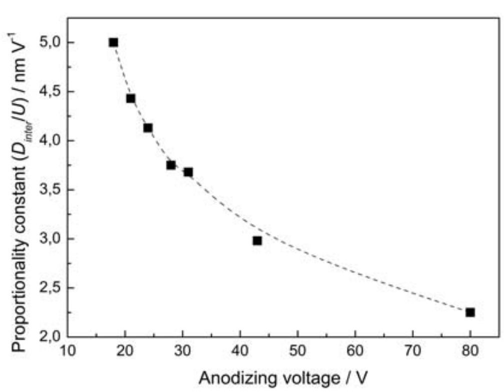

Figure 5. Evolution of the proportionality factor (D_{inter}/U) as a function of anodizing voltage for porous anodic alumina films formed in malonic acid.

The results obtained clearly indicate that, despite the use of electrolytes with different activities for anodizing of aluminum, formation of microstructure of porous films falls under general law. Therefore, there should be some common factor determining parameters of microstructure of porous anodic films during anodizing of aluminum in malonic and oxalic acid. In our opinion, mechanical stresses in alumina for acids with different activities can be such a common factor. This conclusion is confirmed by experimental data on increase in mechanical stress in the oxide surface triggered by an increase in anodizing current [12]. This is also in good agreement with the model for mechanical stress generation during Al anodizing, which takes into account viscous oxide flow and ion migration [13,14].

4. Conclusions

The morphology of nanotextured surface of aluminum films after selective removal of porous anodic alumina films was studied by SEM with subsequent statistical analysis of SEM images by ImageJ software.

The results obtained for anodic films formed in malonic acid in the anodizing voltage range of 15-80 V allowed to determine the linear character of the change in the interpore distance with the anodizing voltage with a slope of 1.45. It was shown that the slope of the curve fully coincides with the slope of same function for anodic films formed in oxalic acid up to 40V. Such a result may indicate that mechanical stress in anodic alumina layer is the main factor responsible for formation of nanoporous structure of anodic alumina films.

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