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The effects of time and temperature on the arrangement of anodic aluminum oxide nanopores

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ABSTRACT

An anodic aluminum oxide was formed by self-organized two step anodization in 0.3 M oxalic acid at four temperatures: 35, 40, 45 and 50 °C and three voltages: 30, 40 and 50 V. Duration of anodization steps was also varied: 30, 60 and 120 min. The influence of electrolyte temperature and duration of anodization on the nanoporous alumina arrangement was studied with three methods: regularity ratio derived from fast Fourier transform intensity profile, averaged regularity ratio evaluated from radial average of fast Fourier transform and defect maps (Delaunay triangulation). It was found that for sufficiently long anodization (60 min or longer) the better arrangement of the pores was obtained at higher temperatures. Additionally, the better arrangement of nanopores was obtained with the longer duration of the anodization step. The present results are rationalized by a phenomenological model and compared with the literature data.

1. Introduction

The anodic aluminum oxide (AAO) which consists of hexagonally arranged nanopores is a nanomaterial fabricated via electrochemical methods. Geometrical features of the nanopores, like the pore diameter, interpore distance, thickness of the porous oxide layer etc. are in a strong relation with operating conditions like the applied voltage, type, temperature and concentration of the electrolyte or duration of the anodization process [1–5]. The AAO is mostly formed in three major electrolytes: sulfuric acid [1,2,6], oxalic acid [1,2,5] and phosphoric acid [1,2,7–9]. The applied voltage relies on the applied electrolyte: the lowest voltages, resulting in the smallest pore diameter and interpore distance, are being applied for sulfuric and oxalic acid [1,2,10–13] and the higher voltages — for phosphoric acid [1,2,8]. Moreover, to overcome this limitations various approaches have been developed like hard anodization [14,15], anodization in non-aqueous electrolytes [9,15] or anodization in electrolytes containing modifiers [12,13].

Due to the geometrical features, the AAO is used as a template for nanofabrication [16]. With the AAO, developments in magnetism of nanomaterials [17–19], renewable energy harvesting and storage [20–24], sensor assembly [16,25–28], improvements in surface enhanced Raman spectroscopy (SERS) [29,30] and biomaterial performance [16,31–33] have been achieved.

For the AAO applications in nanofabrication, very often arrangement of the template is crucial. Routinely, a fast Fourier transform (FFT) is employed to study periodic, self-organized structures, like nanoporous arrays. Typically, researchers are

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conducting three intensity profiles through FFT of the image. The ratio of the intensity maximum to width at the half of the peak height is being used as the measure of the regularity of AAO [34–37]. However, such an approach does not take into account numerous factors affecting the value of so calculated regularity ratio. According to few studies, correction factors have been introduced [15,38]. The most reliable correction factor that takes into account the number of pores on the analyzed images, area of the analyzed surface and porosity, has been introduced for analysis of the AAO formed in oxalic acid by short anodization [39]. In the present paper, this tool will be also employed.

Typically, the AAO is being formed at low temperatures (below room temperature). However, it is a time consuming process because the oxide growth rate decreases with temperature decrease. In this paper, we are focusing on the AAO formed above room temperature which significantly increases the oxide growth rate due to the increase of ionic mobility and electrical conductivity of the electrolyte [5]. Arrangement of the AAO pores is studied to optimize temperature and time of anodization in order to obtain a well-organized AAO at short time (up to 2 h). A few methods of quantitative arrangement analysis have been employed to study the influence of temperature and time on the arrangement of the pores.

2. Materials and Methods

In order to fabricate the AAO, we have followed the procedure reported previously [40]. Briefly, 0.5 cm × 2.5 cm was cut from 99.9995% pure Al foil (Puratronic, Alfa Aesar). Subsequently, the samples were degreased (in acetone and ethanol) and electropolished (4:1 C_2H_5OH:60 wt.% $HClO_4$, 0.5 A/cm^2, 10 °C, 1 min). So prepared samples were sealed with an acid resistant dye in such a manner as to limit working area of the sample to 0.5 cm^2. Nanoporous alumina was formed by a two-step self-organized anodization under constant voltage (20.0 to 60.0 V) in a 0.3 M oxalic acid solution at four temperatures of 35, 40, 45 and 50 °C, and for three various durations of anodization step (30, 60 and 120 min) with Pt grid (5 cm^2) as a cathode. According to the self-organized procedure, after first step of anodization, the grown oxide was chemically removed with 6 wt.% H_3PO_4 and 1.8 wt.% H_2CrO_4 at 60 °C for 90 min. Re-anodization was conducted at the same set of experimental conditions (voltage, temperature, time) as for the first step.

The AAO images were taken with Carl Zeiss Leo 1530 field emission scanning electron microscope.

A fast Fourier transform based quantitative arrangement analysis was performed with a scanning probe image processor WSxM v.5.0 [41,42]. For every set of experimental conditions, the arrangement analysis was done for three images. It means that for regularity ratio nine intensity profiles were taken into calculations and for the averaged regularity ratio three radial averages were taken into account.

Delaunay maps were performed for three images for every set of experimental conditions, hence a defect percentage for a given set of operating parameters is an average estimated from three images.

3. Results and Discussion

3.1. *Influence of Temperature on the AAO Arrangement*

Fig. 1 shows the influence of electrolyte temperature on the formation of AAO. First of all, one notices that the pore diameter increases with increasing temperature (Fig. 1a, e, i and m) which has been reported in detail in [40]. According to the mechanistic studies of AAO growth, temperature should influence the formation of the nanoporous anodic oxide. According to Pashchanka and Schneider [43,44], the AAO steady-state growth is analogous to the Rayleigh–Bènard convection cell formation [43,44]. Of course, the gradient of temperature is substituted here by the gradient of electric field potential, however, analogous to Rayleigh number, criterion number for nanoporous anodic oxide formation also takes into account viscosity, which is of course influenced by temperature [44]. Therefore, one can expect an indirect influence of temperature on the arrangement of anodic alumina. With a temperature increase, evolution of the FFT patterns is observed (Fig. 1b, f, j and n): from a blurred thick ring (35 °C, Fig. 1b) to six distinct dots in the corners of the hexagon (50 °C, Fig. 1n). Also, the intensity of FFT profiles conducted along three major hexagonal directions (Fig. 1c, g, k and o) and radial averages conducted for the whole FFT (Fig. 1d, h, l and p) increases which should translate into a better arrangement of the nanopores. Nevertheless, for a quantitative arrangement analysis, the correction factors taking into account the number of pores (n), analyzed surface area (S) and AAO porosity (α) have to be introduced. Previous study shows that influence of these three quantities on the quantitative arrangement analysis is significant [39]. To estimate the regularity ratio derived from the intensity profiles, the maximum intensity (H) to the width at half the intensity (W) ratio with correction factors has to be applied [39]:

$$R = \frac{(nS)^{-\frac{3}{2}}}{\alpha^2} \cdot \frac{H}{W}. \qquad (1)$$

For most of the anodization durations, one can notice that there is no distinct tendency in the dependency of regularity ratio on electrolyte temperature (Fig. 2). On the one hand, the results are consistent with the results obtained by Zaraska et al. [45] for the AAO formed in 0.3 M oxalic acid at a much lower temperature range: from −1 to 17 °C. Also, no significant influence of electrolyte temperature on the AAO arrangement was noticed. On the other hand, the mechanistic study of Pashchanka and Schneider [44] suggests that there should be some influence of electrolyte temperature. To judge this discrepancy, other tools must be employed. The FFT-based regularity ratio has numerous advantages, including a rapid quantification of the periodic structure arrangement. However, the presented approach has one major disadvantage, namely, that it takes into consideration only three major directions of the FFT, which are additionally manually selected. Thus, this tool is insufficiently sensitive for such small changes.

To overcome this issue, in this research the averaged regularity ratio, derived from the FFT radial average, taking all the directions into the estimations, was employed. The averaged