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Ultra-small nanopores obtained by self-organized anodization of aluminum in oxalic acid at low voltages

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ABSTRACT

A simple method of fabrication of anodic aluminum oxide at low voltages (from 5 to 15 V) in 0.3 M oxalic acid is presented. To overcome the issues concerning the anode's burning, a high velocity stirring was applied. It allowed to achieve nanopores with ultra-small diameters (even 12 nm), interpore distance (even 31 nm) and tremendously high pore densities (up to 980 pores per 1 μm^2) with simultaneous high porosity (up to 38%). Moreover, the presented approach (no modifier added to the electrolyte) resulted in the AAO with relatively well arranged ultra-small nanopores.

1. Introduction

Recently, nanoporous anodic aluminum oxide (AAO) is one of the most commonly fabricated material with electrochemical techniques, due to its applications in template assisted nanofabrication [1]. It allows to fabricate hexagonally-arranged nanostructures made of diverse materials with emerging innovative properties owing to their small size.

Close-packaging of anodic alumina ultra-small nanopores would be advantageous for template assisted fabrication methods. It would allow to obtain nanowires, nanotubes and nanodots with ultra-small diameters and enhanced properties linked to their dimensions. Pore diameter and interpore distance decrease linearly with anodizing voltage decrease. To obtain pores with possibly smallest diameters and interpore distances the lowest voltages have to be applied. Typically, the most suitable electrolyte for AAO formation with small pores is sulfuric acid and voltage ranging from 15 to 25 V [2]. The resulted pore diameter and interpore distance range from 20 to 25 nm and 44 to 65 nm, respectively. Ding et al. anodized aluminum in sulfuric acid at 10 V and obtained AAO with average pore diameter of 7.9 nm and interpore distance of 26.2 nm. In this case modifiers like aluminum sulfate and citric acid were added to the electrolyte to prevent anode from burning (anodic dissolution) at low voltages [3]. These results have been even commercialized [4].

The major issue undertaken in this research is fabrication of anodic alumina with small nanopores via self-organized anodization in oxalic acid and investigation of the influence of operating conditions on geometrical features of the nanopores. In our study, a simple method of fabrication of anodic aluminum oxide is presented—to overcome the issues linked to the anode's burning, a high velocity stirring was applied and no modifiers were added to the electrolyte.

2. Materials and methods

A high-purity 0.25 mm aluminum foil (Alfa-Aeasar) was cut into coupons (5.0×25 mm^2). Next, aluminum was degreased in acetone and ethyl alcohol. Further, electropolishing was conducted in 1:4 volume mixture of 60% perchloric acid and ethyl alcohol. Platinum grid (6 cm^2) was applied as a cathode, current density of the process was 0.5 A/cm^2 and it lasted for 1 min. After electropolishing, the aluminum specimens were coated with acid-resistant paint at the back and edges to prevent sample from "burning" during anodization. Working area of aluminum was 0.5 cm^2. First step of anodization was conducted in 0.3 M oxalic acid at three different voltages (5.0, 10.0, and 15.0 V) and three different values of temperature (20, 30, and 40 °C). To prevent anode's burning, the solution during anodization was vigorously stirred (1000 rpm). Due to the high velocity stirring, local temperature and current density inhomogeneities, leading to anode's burning, have been minimized. Duration of the process was 30 min. Subsequently, as formed alumina was chemically removed in a stirred mixture of 6 wt% phosphoric acid and 1.8 wt% chromic

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acid at 60 °C for 60 min. Next, aluminum was re-anodized at the same conditions as present during the first step of the process. The characterization of the nanoporous alumina was performed by using the Carl Zeiss Leo 1530 field emission scanning electron microscope (FE-SEM). The fast Fourier transform (FFT) of the FE-SEM images were calculated by using a scanning probe image processor WSxM v 5.0 [5,6]. Image analyses (pore diameter and pore density) were done with NIS-Elements AR 3.10 programme purchased from Nikon Company. Average pore diameter was evaluated from about 5.000 independent measurements for a given operating conditions of the process. Pore density (number of pores occupying 1 μm^2) was estimated from six FE-SEM images of the same sample anodized at given operating conditions. Interpore distance was evaluated from FFT as an inverse of a radial average of the FFT image of six FE-SEM images.

3. Results and discussion

FE-SEM images of alumina formed at 30 °C in 0.3 M oxalic acid at low voltages show closely packed nanopores with small diameters (Fig. 1). Depending on temperature and voltage, pore diameter was ranging from 12 to 28.7 nm. It was found, that pore diameter increases linearly with voltage, as also observed in the application of higher voltages (Fig. 2a) [2]. Also temperature increase, enhancing reaction between the grown oxide and acidic

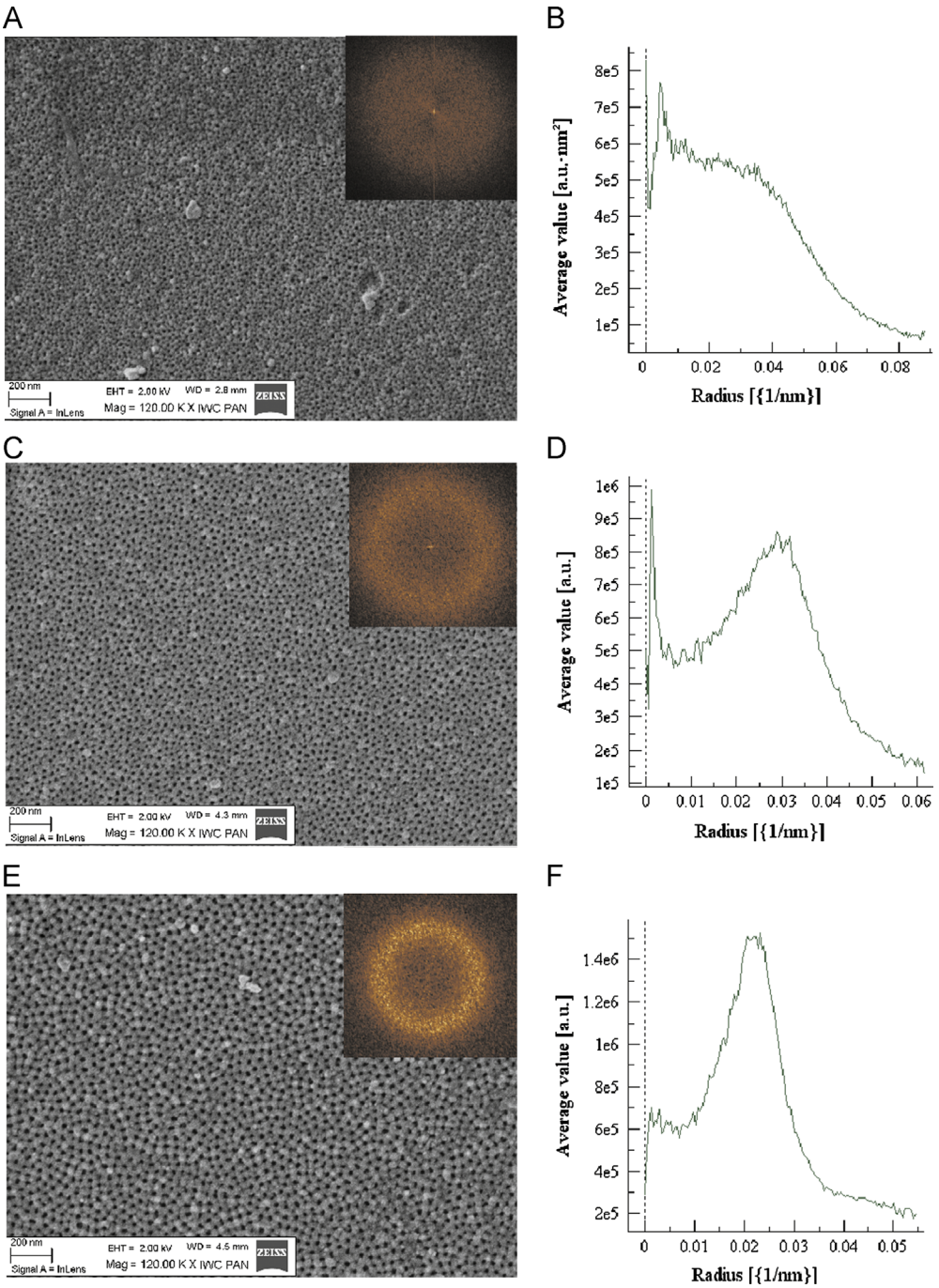

Fig. 1. FE-SEM micrographs with FFT images with their radial averages for aluminum anodized for 30-min in oxalic acid at 30 °C. Anodizing voltages was 5.0 V (A) and (B), 10.0 V (C) and (D) and 15.0 V (E) and (F).