



A novel nanostructure with hexagonal-prism pores fabricated under vacuum circumstance



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ABSTRACT

It is well known that electrochemical anodizations of valve metals are performed under the normal pressure (1 atm = 0.1 MPa), and only columnar pores could be usually obtained in porous anodic alumina (PAA). So far, there have been very few reports involving the atmosphere pressure and its effect on the nanostructure of PAA. Here, a novel PAA nanostructure with hexagonal-prism pores has been successfully fabricated under a vacuum system (0.01 MPa), and its forming process is clarified by the anion-contaminated alumina model and oxygen bubble mold. The present results can provide unique insights into the inherent relations between the structural features and anodizing parameters in all anodizing process.

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1. Introduction

Self-organized porous nanostructures of valve metal oxides have been extensively investigated due to their various applications [1–3]. The formation mechanisms and fabricating methods of porous anodic alumina (PAA) and porous anodic titania (PAT) have received considerable attention until now [4–8]. In order to fabricate various nanostructures, many techniques have been utilized, such as the well-known two-step anodization [4,9], hard and pulse anodization [4,10] and changing the anodizing parameters or electrolyte composition [4,11,12]. However, as Hebert et al. [8,13] indicated, no model has successfully explained the relationships between film morphology and processing parameters. And the influence of processing parameters (e.g., temperature, time, anodizing voltage and rotation rate) on the film morphology has been studied extensively [11–14]. However, the influence of atmosphere pressure on the film morphology has been ignored, because the pressure has no direct contribution to the film morphology according to the classical theories of pore formation mechanism [4,7,8,15–18]. All above anodizing processes were performed at the normal atmosphere (0.1 MPa). In fact, the pressure of electrolytic bath could influence the PAA morphology [19]. Moreover, the structural features of PAA and anion-contaminated

alumina (ACA) layer around the pore walls have not been successfully elucidated so far [4,8,18,20,21].

We have proposed a new growth model of PAA, which emphasizes the close relationships among pore generation, ACA layer and oxygen bubble mold (OBM) [22,23]. In our latest work, a two-tier nanostructure with narrow mouth and wide abdomen has been successfully fabricated [12], which was clarified by the combination of viscous flow model [13,18] and oxygen bubble mold.

Herein, in order to demonstrate the influence of oxygen evolution on the PAA morphology, two anodizing processes of aluminum under the normal pressure and vacuum system were investigated by comparison. As a result, a novel nanostructure with hexagonal-prism pores is first assembled by anodization under a vacuum system. These hexagonal-prism pores help to identify the dominating factors of pore generation and development. Based on the ACA model [20,21] and the OBM model [12,22,23], the forming process of the hexagonal-prism pores is discussed in detail. This new anodizing technology under vacuum system should be particularly useful for assembling special nanostructures.

2. Experimental

Aluminum (99.99%) sheet of 0.2 mm thickness was employed. The sheet was dipped into 2 wt% NaOH solution at 70 °C for chemical polishing for 120 s and then electropolished at a constant current density of 120 mA cm⁻² for about 90 s in an electrolyte composed of phosphoric acid (80 wt%), chromium trioxide

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(12 wt%) and water (8 wt%) at 70 °C. The electropolished sheets were anodized in an ethylene glycol solution containing 6 wt% phosphoric acid at constant current (15 mA cm⁻²) and the room temperature for 3600 s under two different pressures (0.1 MPa and 0.01 MPa). A digital thermometer (through a thermocouple) was used for measuring the temperature of the electrolyte. No stirring and cooling devices were adopted and the temperature rise of the electrolyte was less than 23 °C. The nanostructure was characterized by field-emission SEM (Hitachi S4800). To get the cross-section images, the anodized samples with Al substrate were bent into V-shape before observation.

3. Results and discussion

Fig. 1 shows the micrographs of the nanostructure with hexagonal-prism pores in PAA obtained under vacuum condition (0.01 MPa). There are many hexagonal and polygonal pores in Fig. 1a. Only a few columnar pores, which have small pore-diameter and thick pore-wall, can be seen in Fig. 1a. This nanostructure was obtained by anodization under a vacuum system (0.01 MPa). However, different nanostructure with columnar pores in PAA anodized under the normal pressure (0.1 MPa) was obtained as shown in Fig. 2a and b. There are significant differences between Figs. 1a and 2a. Obviously, besides hexagonal-prism and columnar pores, the pore-diameter and pore-wall are very different. The diameters are ~270 nm and ~100 nm in Figs. 1b and 2b, respectively. According to the classical growth models of PAA (e.g., field-assisted dissolution model, volume expansion model and self-organized model) [4,15–18], it is obviously hard to explain the above differences. Because other anodizing conditions (e.g., electrolyte, temperature, anodizing current or voltage and time) are all the same except for the system pressure, these significant differences may be attributed to the different pressures in two anodizing systems, which can be clarified by the ACA model and oxygen evolution in the following text.

In fact, when pure aluminum was anodized in 6 wt% H₃PO₄ ethylene glycol solution under the normal pressure (0.1 MPa), the evolution of oxygen bubbles on the anode and H₂ bubbles on the cathode could be observed easily by the naked eyes, and Fig. 2c shows the difference of the bubbling gas between the anode and the cathode. Fig. 3 shows the difference of the bubbling gas on the anode under different pressures (0.1 MPa and 0.01 MPa) and at different moments. Fig. 3a and b show the different distributions of oxygen evolution around the anode at different moments under

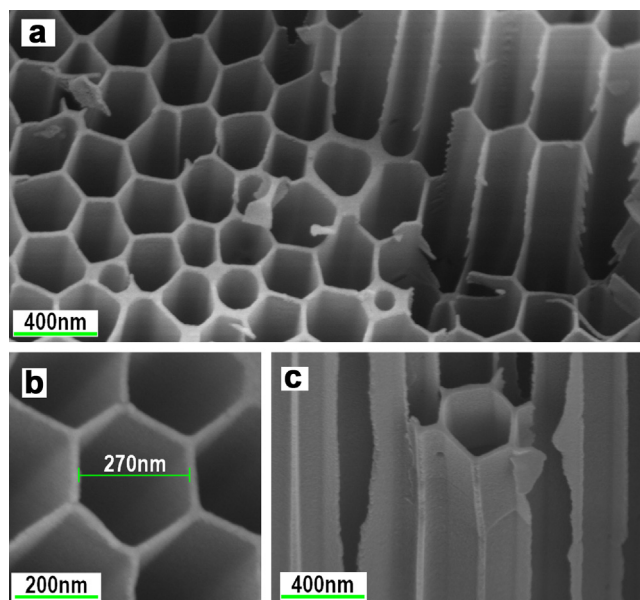


Fig. 1. SEM images of the nanostructure with hexagonal-prism pores in PAA anodized for 3600 s under 0.01 MPa.

0.1 MPa. For the same anodizing process under a vacuum system (0.01 MPa), oxygen evolution became very intense and much more oxygen bubbles could be seen in Fig. 3c and d. Fig. 2d shows the voltage-time curves of the anodizing processes under 0.1 MPa and 0.01 MPa. Under the vacuum circumstance, intense gas bubbles will alter the electrical conductivity in the pores. The variation of bubble quantity can result in the change of anodizing voltage. Therefore, the voltage under 0.01 MPa is higher than that under 0.1 MPa.

We consider that the hexagonal-prism pores in Fig. 1 result from both intense oxygen evolution and the existence of ACA layer around the columnar pore walls. In fact, the porous layer of PAA is composed of two structurally different regions, anion-free pure alumina and ACA layer [4,20,21], as shown in Fig. 4a. The ACA layer was first described in detail by Thompson and Wood [20]. Diggle et al. [24] considered that anions incorporation into the barrier oxide was closely associated with the degree of pore formation. However, this important viewpoint has been ignored for many years, because the existence of ACA layer is contrary to

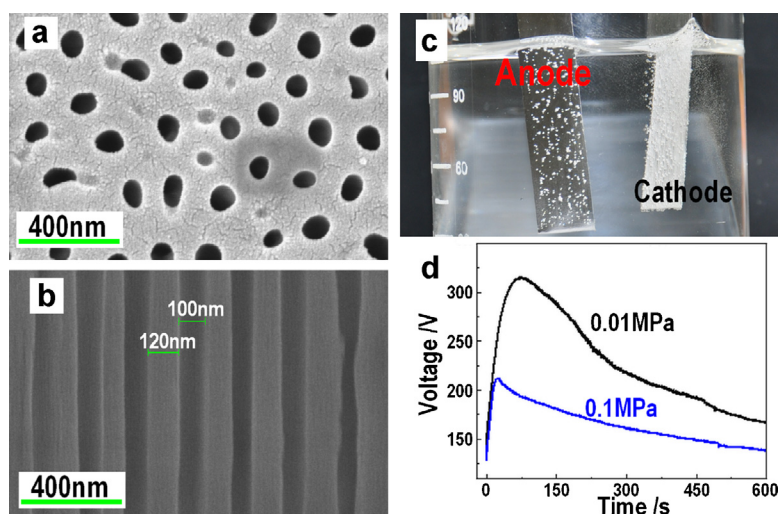


Fig. 2. SEM images of the surface morphology (a) and the cross section (b) of the nanostructure with columnar pores in PAA anodized for 3600 s under 0.1 MPa. (c) Photograph showing the gas bubbles around the anode and the cathode under 0.1 MPa. (d) Voltage-time curves of the anodizing processes under 0.01 MPa and 0.1 MPa.

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