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Three-Dimensional Networked Nanoporous Anodic Alumina Films with Vertical and Transverse Pores Fabricated on Al with Different Purity

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Introduction. Porous Alumina films with ordered parallel nanopore arrays obtained from Al anodization are widely used as nano-templates to fabricate various one-dimensional (1D) nanostructures like nanowires and nanotubes for many applications such as perpendicular magnetic recording media, photocatalysis, electrode catalysts, solar energy conversion, etc.[1] However, most of studies so far adopted highly pure Al as high as more than 99.99% as starting materials to seek for highly ordered porous structures. Since the highly pure Al materials are high-cost and lack of satisfied mechanical strength, it is desirable to utilize low-pure Al or Al alloy materials with relatively low costs in fabricating nanoporous alumina nanostructures for various practical applications. Recently, much effort has been done to fabricate tailored nanoporous alumina films with varying pore diameters gradually or step-wisely by means of changing anodizing voltages or current density, electrolytes, temperature, etc.[2-4] This investigation reports a simple anodizing method to fabricate a novel three-dimensional (3D) networked porous anodic alumina nanostructure from various industrial pure Al materials. The effects of purity and alloy elements in Al substrate materials were investigated and a possible mechanism was proposed.

Experimental. As starting materials, four kinds of aluminum sheets (20 x 50 mm) in purity of 99%, 99.3, 99.56, and 99.999% were used as received. Before anodizing, the specimens were electrochemically polished in a mixed solution of 70% $HClO_4$ and 99.5% ethanol in a ratio of 1:4 at 25 V and 280 K for 2 min. The anodization was performed in solutions of 0.9M phosphoric, 0.3M oxalic, and 0.7M sulfuric acid at 15 – 190 V and 273 – 288 K from 10 min to 5 h.

The morphology of the anodized specimens were observed by FE-SEM, and the composition and chemical states of the Al substrate materials and the porous alumina films were analyzed by EDS, GDOES, and XPS.

Results and Discussion. Fig. 1a shows a representative porous alumina film with a unique porous structure, which was formed by anodizing Al sheet with a low purity in 99.0%. It can be clearly seen that, apart from the large parallel pores (ϕ250 nm) perpendicular to the film/metal interface, numerous transverse pores with small sizes in ϕ50 – 80 nm were also formed across the pore walls with a regular spacing in 220 nm. The transverse pores distributed throughout the alumina pore walls except for the barrier layer, thus making all of the pores connected into a nanoporous network, *i.e.*, a 3D porous nanostructure. As a reference, a conventional two-dimensional (2D) porous alumina film formed on a highly pure Al sheet in 99.999%Al was given in Fig.1b, in which highly ordered but independent pores in ϕ180 nm were formed along the electrical field as usual.

It was found that the formation of transverse pores was easier on low pure Al than on the highly pure one, irrespectively of anodizing voltages and solution concentrations. The generation and growth of the transverse pores can be mainly ascribed to the chemical dissolution of impurities like Cu, Fe, and Zn components in Al materials, due to the corrosive nature of phosphoric acid electrolyte and/or the electrochemical dissolution driven by the electrical field during the anodization.

Fig.2 shows the effects of Al purity on the films thickness and pore intervals for the porous alumina films formed in a phosphorous acid solution under 160 V for 5 h. The thickness of porous alumina films decreased greatly with the decrease the purity, which may be attributed to the low corrosion resistance for the alumina films with more impurities. On contrast, the variation of the purity of Al materials showed little effect on the pore intervals and the barrier layer thickness (not shown), indicating the identical insulating nature for the anodic alumina films.

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4) C. Cheng, and A. H. W. Ngan, *Nanotechnology*, 24, 215602 (2013).

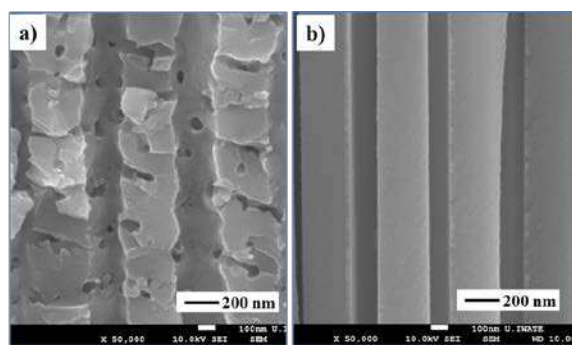

Fig.1 Fracture cross-sectional FE-SEM images of porous alumina films formed in a phosphorous solution at 160 V from Al sheets of (a) Al-99.0% and (b) Al-99.999%.

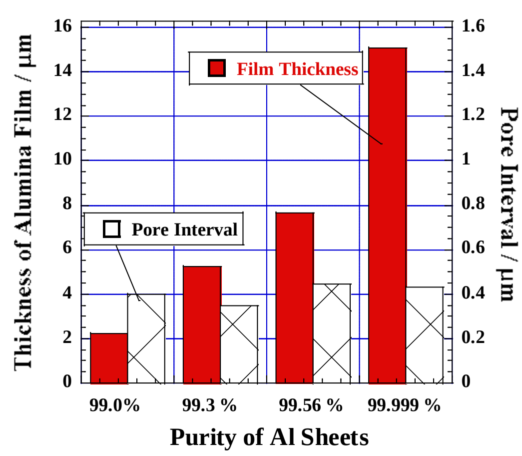

Fig.2 Effects of purity of Al sheets on the formation rates and the pore intervals of porous alumina films.