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Impurity-driven defect generation in porous anodic alumina

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ABSTRACT

We report that the morphologies of porous anodic alumina films are affected significantly by the presence of small amounts of copper impurity in the aluminium substrate, resulting in generation of defects during anodizing in phosphoric acid over a wide range of conditions. The copper is accumulated at the metal/film interface and transported preferentially to triple points of the alumina cells, where oxygen gas is generated leading to development of gas-filled voids.

1. Introduction

Porous anodic alumina (PAA) attracts much fundamental and commercial interest due to its unique self-ordered morphology [1]. The major morphological parameters, e.g. pore diameter and inter-pore distance, may be adjusted precisely by selection of the anodizing conditions, with a high degree of hexagonal self-ordering achieved by two-step anodizing or by preconditioning the aluminium surface [2,3]. Perfection of the PAA morphology is an important factor that has defined potential key applications of the PAA matrix, including template-based synthesis of nanomaterials and photonic crystals [4,5]. Further, various approaches have been developed to modify the morphology of PAA for particular applications, e.g. by a combination of mild and hard anodizing of pre-patterned aluminium [6] or use of oscillatory currents, followed by chemical etching [7]. However, other studies have revealed that the preferred anodizing conditions can promote formation of void-like defects, which can disrupt the highly ordered porous matrix [8–10]. Considering the potential for enrichment of specific alloying elements at the metal/film interface during anodizing, through preferential oxidation of aluminium [11,12], and oxide plasticity and flow during PAA growth [13], we propose new insights into the origin of defects.

2. Experimental

Porous anodic films were formed on electropolished aluminium foil (99.99% purity, containing 30 Cu, 20 Fe, 20 Si (ppm)) either at constant voltages of 60 to 178 V or at a constant current density of 5 mA cm^{-2} in phosphoric acid (0.01 to 1.2 M) at room temperature, with pore widening of selected films in 50 vol.% phosphoric acid. Films were also grown on aluminium and an Al–Cu alloy (≤0.05 at.% Cu), produced by magnetron sputtering using a 99.999% Al target and co-sputtering of 99.999% Al and Al–1 at.% Cu targets respectively.

Fracture sections of the films were observed in Hitachi S-806 and Zeiss Ultra 55 scanning electron microscopes (SEM). Films were also examined in plan-view and in cross-section in a JEOL 2000 FX transmission electron microscope (TEM); for plan views, stripped films were thinned by an argon ion beam using a Gatan (Model 691) precision ion polishing system, while cross-sections were prepared using a Leica Ultracut UCT ultramicrotome.

3. Results and discussion

A cross-section of the porous film formed on 99.99% aluminium at 170 V in 0.01 M phosphoric acid electrolyte illustrates the presence of periodically separated defects along the length of the cell material (Fig. 1a). The defects were present in all pores throughout the film thickness. Further scrutiny of the cell material reveals circular features at cell boundaries, with occasional disturbances to the pore walls also evident (Fig. 1b). After pore widening from 80 to 180 nm, numerous cavities of ~70 nm diameter and ~200 nm separation appear in the pore walls (Fig. 1c). Occasional, non-circular voids are also evident adjacent to the pores. Examination of the scalloped metal/film interface indicates that defects originate in the barrier layer of the film above the metal ridges, as indicated by the arrow in Fig. 1d. Similar, though less numerous, defects are observed in a film formed at 60 V in 0.3 M phosphoric acid (Fig. 1e).

Observation of a plan-view of the film formed to 170 V in 0.01 M phosphoric acid suggests that the defects are located at triple-point junctions where neighbouring cells meet (Fig. 2a); the defects were

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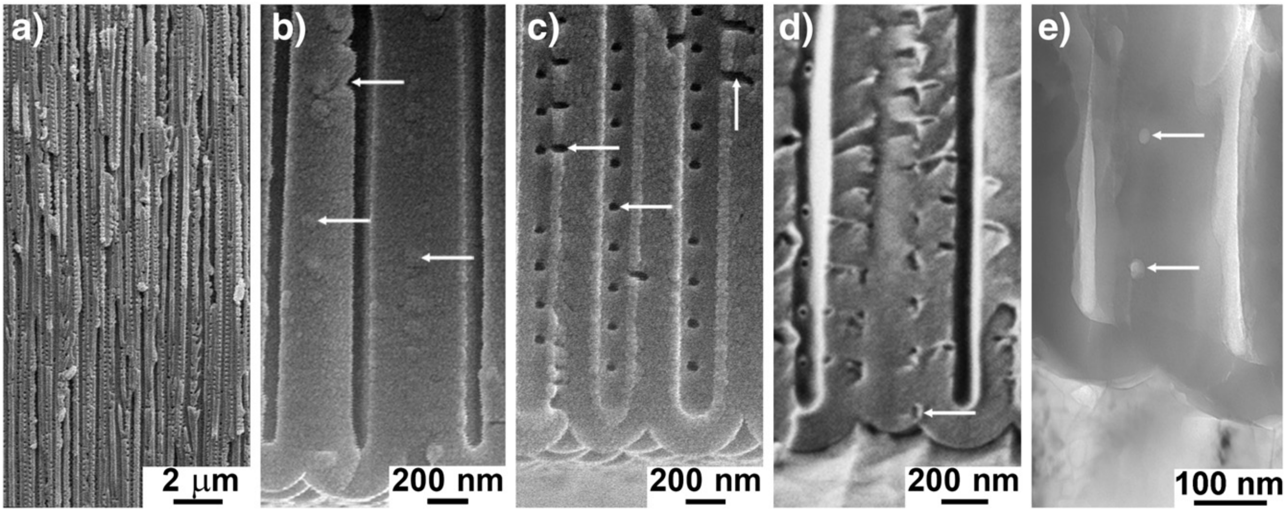

Fig. 1. Cross-sectional views of PAA formed at different voltages on 99.99% aluminium in 0.01 M phosphoric acid electrolyte obtained by (a–d) scanning and (e) transmission electron microscopy: (a) section through the thickness of the film formed at 170 V; (b) enlargement of (a) showing barrier layer and adjacent porous region; (c) as (b) but after pore widening to reveal defects; (d) section of the barrier layer region of the film formed at 178 V showing a defect in the alumina located above a metallic ridge at the metal/film interface; (e) section of barrier layer region of the film formed at 60 V revealing a decreased population of the defects. Arrows indicate circular-shaped features and individual disturbances in (b) and individual defects in (c), (d) and (e).

exposed near the film surface by a phosphoric acid etch. Examination of an ion-beam-thinned film formed at 140 V in 0.3 M phosphoric acid shows an irregular cell structure with an average cell size of ~330 nm and pore diameter of ~160 nm (Fig. 2b). Cell boundary bands, comprising alumina free of incorporated phosphorus species, are evident as dark, approximately hexagonal-shaped features in the image, as shown previously [14]. Individual defects appear as a circular-shaped feature at triple-point junctions, generally, but not always, extending toward the pore wall in the form of three tubular branches; clearly, circular holes result when the branches intersect the pore walls. Observations of films formed at reduced voltage (Fig. 2c) suggested more limited development of tubular defects. Scrutiny of the micrographs of Fig. 2b–c reveals the presence of defect initiation sites at all triple-point junctions, with no evidence of initiation elsewhere in the film.

Growth of porous films occurs at the metal/film interface by inward migration of oxygen ions through the barrier layer, with outwardly mobile aluminium ions being ejected into the electrolyte at the pore base. The formation of anodic alumina occurs through the reaction:

$$2\mathrm{Al} + 3\mathrm{O}^{2-} \rightarrow \mathrm{Al}_2\mathrm{O}_3 + 6\mathrm{e}. \tag{1}$$

Evidence from studies of barrier films on solid-solution Al–Cu and Al–Cr alloys indicates that oxygen evolution may accompany alumina formation in the presence of the alloying elements [15,16]. The alloying element first enriches in the alloy at the metal/film interface and, upon achieving a sufficient enrichment, oxidizes and migrates across the anodic film, with generation of oxygen commencing within the film by the reaction:

$$2\mathrm{O}^{2-} \rightarrow \mathrm{O}_2 + 4\mathrm{e}. \tag{2}$$

The anodizing of alloys suggests a pivotal role of impurities in the generation of defects in porous films, with the following mechanism

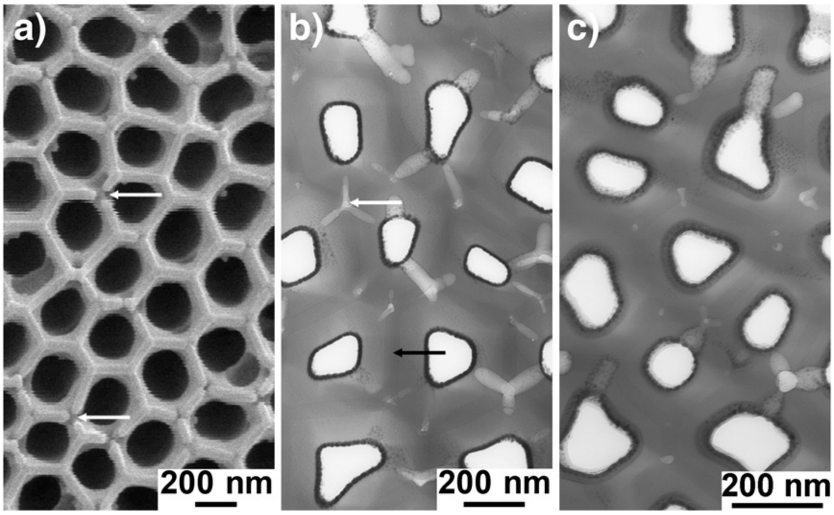

Fig. 2. Plan views of surface and bulk regions of PAA formed on 99.99% aluminium: (a) scanning electron micrograph of the surface of a film formed at 170 V in 0.01 M phosphoric acid, revealing defects at triple point junctions where neighbouring cells meet; transmission electron micrographs of an ion-beam-thinned film formed (b) at 140 V in 0.3 M phosphoric acid and (c) at 5 mA cm^{-2} in 1.2 M phosphoric acid (with a steady voltage of 100 V during porous film growth) revealing defects with tubular branches at triple points. White arrows in (a) and (b) indicate defects at triple point junctions; the black arrow in (b) shows an inner region of a cell, free of electrolyte-incorporated species, with a relatively dark appearance.