

New Insights into Pore Initiation in Anodic Alumina

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Porous anodic films are of great importance to the protection of aluminium alloys against corrosion and wear. The films are composed of amorphous alumina permeated by fine, cylindrical pores that extend from the film surface almost to the metal substrate. A much thinner, non-porous barrier layer separates the pores from the metal, as shown in the example of a transmission electron micrograph of a porous film that was formed in a phosphoric acid electrolyte, presented in Figure 1. Over the last fifty years, the growth of the films and the formation of the pores have usually been explained by a field-assisted dissolution model. In this model, the anodic alumina is formed at the metal/film interface due to migration of O^{2-} ions across the barrier layer. The migration takes place under a high electric field at the barrier layer, which is established by the external power supply in the electrolytic cell. At the same time that the oxide is formed, dissolution occurs at the pore base, such that the barrier layer remains of constant thickness. The dissolution is vastly

accelerated in comparison with the usual chemical dissolution of the film in the electrolyte, which is attributed to the effect of the electric field at the pore base.

There has been a resurgence of interest in porous anodic films, partly due to the interest in potential applications in nanotechnology, but also for the development of new processes that can eliminate the need for anodizing in chromic acid, which is an often favoured process for aerospace applications, but which is now under legislative pressure due to environmental and health reasons. Within the LATEST Portfolio Partnership and LATEST2 programmes, alternative anodizing processes have been investigated in detail, coupled with fundamental research into the growth mechanism of the films. The latter has led to a re-evaluation of the mechanism of pore formation. Firstly, using tungsten tracers, it was shown that the pore growth involves flow of oxide within the barrier layer, with field-assisted dissolution having a minor or negligible role under many conditions of film growth. Thus, as new oxide is added at the base of the barrier layer, oxide within the barrier layer is pushed toward the pore walls due to the stresses associated with the film growth. The oxide is made plastic due to the ionic transport processes within the barrier layer that involve migration of both Al^{3+} and O^{2-} ions.

In more recent work, attention has been directed toward the initiation of pores and for this purpose a new tracer approach was developed using arsenic species, which do not migrate during the film growth. The arsenic is introduced into the film by a first stage of anodizing in sodium arsenate electrolyte. The aluminium is then further anodized in a phosphoric acid electrolyte. Figure 2(a) shows transmission electron micrographs and elemental maps of the film at an early stage of re-anodizing, before the pores have initiated. The arsenic is revealed to be buried slightly below the film surface, and phosphorus species are also present in the outer region of the film. Figure 2(b) shows the film at later stage, when the main pores of the film have begun to form. The arsenic map discloses a thin band of arsenic within the barrier layer at the base of the pore. The distribution of the arsenic can be explained by the flow of oxide inward from the original surface of the film. Figure 3 shows schematically the progress of pore development in the anodic alumina film, and the displacement of the arsenic by the flow of oxide. This is the first time that such a process has been demonstrated experimentally. The new tracer approach is currently being further applied to examine pore formation under a range of conditions of film growth, including anodizing in chromic acid which results in a different pore morphology. It also has a potential for application to studies of pore formation in oxides other than porous alumina.

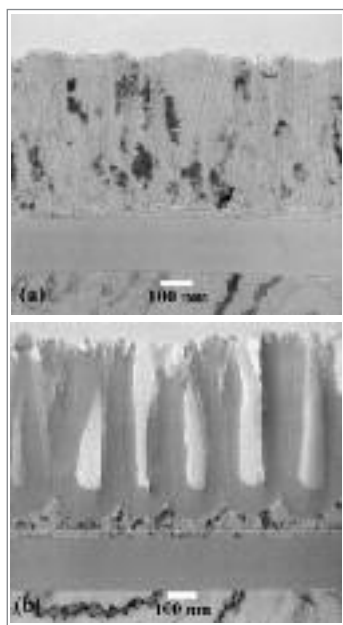


Fig. 1 Transmission electron micrographs of a porous film formed in phosphoric acid on a thin layer of sputtering-deposited aluminium. (a) The original aluminium layer on top of an amorphous layer of anodic alumina. (b) The porous film.

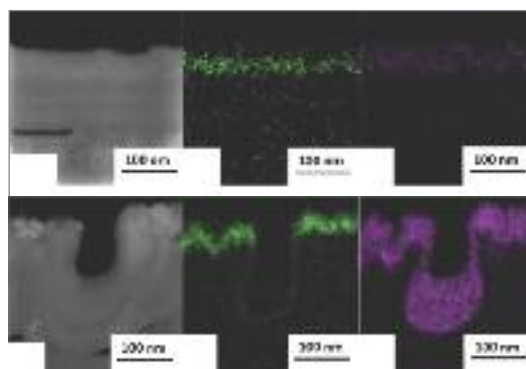


Fig. 2 High angle annular dark field scanning transmission electron micrographs and energy-dispersive X-ray SDD spectrum images of arsenic and phosphorus obtained from a cross-sectioned specimen of aluminium following anodizing to 60 V at 5 mA cm⁻² in 0.1 mol dm⁻³ sodium arsenate electrolyte at 296 K and re-anodizing at 110 V in 0.4 mol dm⁻³ phosphoric acid electrolyte at 296 K for (a) 15 s and (b) 180 s.

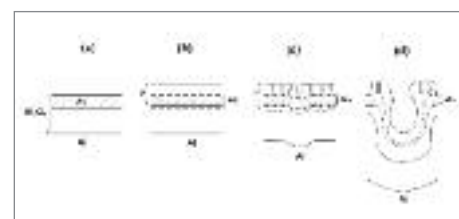


Fig. 3 Schematic diagrams of the formation of anodic films on aluminium. (a) Barrier film formed to 60 V at 5 mA cm⁻² in 0.1 mol dm⁻³ sodium arsenate at 296 K, showing incorporation of arsenic species. (b) Barrier film formed after re-anodizing the specimen depicted in (a) for ~15 s at 110 V in 0.4 mol dm⁻³ phosphoric acid at 296 K, showing the burial of the arsenic. (c) Nucleation and growth of incipient pores and nucleation of a major pore in the film of (b) following further anodizing in the phosphoric acid. (d) Growth of the major pore. Arsenic species are retained in the film and transported inward by plasticized film.

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