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Tracer studies of anodic films formed on aluminium in malonic and oxalic acids

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Abstract

Using a tungsten-containing layer, incorporated into sputtering-deposited aluminium, as a tracer, the growth of porous anodic films in malonic and oxalic acid electrolytes has been investigated using transmission electron microscopy, Rutherford backscattering spectroscopy and nuclear reaction analysis. Comparisons were also made with films formed in phosphoric acid electrolyte, which have been studied previously. The findings reveal a distortion of the tracer layer within the barrier region of the porous films, evident as a lagging of the tracer beneath the pores relative to that in the adjacent cell wall region. Further, the films are significantly thicker than the layer of metal consumed during anodizing and display smooth-sided pores. The anodizing behaviours are consistent with a major role for field-assisted flow of film material within the barrier layer in the development of the pores.
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1. Introduction

Porous anodic films are important to the protection of aluminium alloys against wear and corrosion. Although they have been used for many decades in a wide variety of practical applications, there is still considerable uncertainty about the precise mechanism of film formation [1]. The classical porous film formed on relatively pure aluminium and some compositions of aluminium alloy consists of equal-sized cells of amorphous anodic alumina of hexagonal section, with a cylindrical pore at the centre of each cell [2,3]. The cells are aligned vertically with respect to the metal in a close-packed arrangement. The base of each cell is approximately hemispherical and a thin barrier layer of anodic alumina separates the pore from the metal. In contrast to this regular film morphology, in the presence of certain alloying elements, notably copper among those commonly used, the pore paths through the film can be highly tortuous [4]. The thickness of the porous film is dependent primarily upon the charge passed

during anodizing, while that of the barrier layer is determined mainly by the applied voltage, with a ratio of about 1 nm V^{-1}.

Porous anodic films are usually formed in acidic solutions, although alkaline solutions can also be employed. In such kinds of solution, alumina has a limited solubility and the formation of pores is commonly attributed to an accelerated dissolution due to the high electric field at the pore base/electrolyte interface [3,5]. Under anodizing conditions that result in a constant rate of film growth, the rates of oxidation of the metal and field-assisted dissolution of the film achieve a dynamic balance so that the barrier layer remains of constant thickness. Within the barrier layer, Al^{3+} and O^{2-} ions migrate outward and inward, respectively, with the former being ejected to the electrolyte at the pore base while the latter result in film growth at the metal/film interface [6,7]. In addition to the main alumina species, anodic films can be contaminated by species derived from the characteristic anions of the electrolyte [8,9]. These species are inward migrating at a slower rate than the O^{2-} ions and hence, they do not reach the metal/film interface [10].

The authors have recently developed a tracer approach to the investigation of porous film growth that utilizes a thin tungsten-rich layer incorporated into a sputtering-deposited aluminium substrate [11]. The tungsten layer is then observed during the

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stages of anodizing. Two types of behaviour have been disclosed depending upon the composition of the electrolyte. For electrolytes that produce films with negligible anion contamination the following are found [12,13]: (i) the tungsten layer is incorporated into the anodic film and migrates through the barrier region with no unexpected changes in the shape of the layer, i.e., the layer remains essentially similar in shape in the metal and anodic film; (ii) tungsten species are lost to the electrolyte when they reach the base of pores; and (iii) the thickness of the anodic film is similar to the thickness of the oxidized aluminium. In contrast, for electrolytes that produce films with significant anion contamination, the following are observed [14–16]: (i) the shape of the tungsten layer is strongly distorted during transport through the barrier layer; (ii) no tungsten species are lost to the electrolyte and (iii) the thickness of the anodic film is much greater than the thickness of the oxidized aluminium. These differences in behaviour have been interpreted as reflecting a dominant role for field-assisted dissolution of the anodic alumina in the development of pores in the case of electrolytes of the first type, while for those of the second type, field-assisted film plasticity and deformation of the film under growth stresses play a key role in the formation of the pores. In the present study, the tracer approach is extended to anodic films formed in oxalic and malonic acids. The findings indicate behaviour in the latter category.

2. Experimental

Aluminium, with an incorporated tungsten-rich layer, was sputtering deposited onto anodized aluminium substrates in an Atom Tech system, using targets of 99.999% aluminium and 99.95% tungsten. The substrates had been anodized to 150 V at 5 mA cm^{-2} in 0.1 M ammonium pentaborate electrolyte to form a 180 nm-thick barrier layer. The system was first evacuated to 3×10^{-5} Pa, with sputtering then carried out in 99.999% argon a 5×10^{-1} Pa. The tungsten target was operated briefly mid-way through the deposition, in conjunction with the aluminium target, to form the tungsten-rich layer in the middle of the aluminium deposit. The total thickness of the aluminium was typically ∼750 nm thick. The tungsten-rich layer contained about 20 at.% W. Three thicknesses of tungsten-rich layer were investigated, ∼5, 20 and 50 nm. After deposition, substrates and deposited layers were masked with lacquer to provide specimens with a working area of about 2 cm^2. The specimens were then anodized for selected times at 5 mA cm^{-2} in 0.4 M oxalic acid or 0.3 M malonic acid at 293 K. For comparison purposes, specimens were also anodized in 0.4 M phosphoric acid, which has been used in previous work [11,14,15]. Voltage–time responses were recorded during anodizing. The responses are presented on a relative time scale, derived by dividing the time of anodizing by the time to complete the oxidation of the deposited aluminium. Following anodizing, all specimens were rinsed with de-ionized water and dried in cool air.

Specimens were examined by transmission electron microscopy (TEM) in a JEOL FX 2000 II instrument, using ultramicrotomed sections of 10 nm nominal thickness. Com-

positions were determined by Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA), using ion beams produced by the Van de Graaff accelerator of the University of Paris. For RBS, a 1 mm-diameter beam of 1.9 MeV He$^+$ ions was incident along the normal to the specimen surface, with scattered ions detected at 165° to the direction of the incident beam. The data were interpreted using the RUMP program. The amounts of aluminium and tungsten in the deposited layer and anodic film were determined to an accuracy of ∼5%. However, the relative amounts of tungsten before and after anodizing were accurate to ∼3%. For NRA, a 1 mm-diameter beam of 0.87 MeV ^{2}H$^+$ ions was employed, with emitted protons detected at 150° to the direction of the incident beam. A mylar film in front of the detector stopped elastically scattered ^{2}H$^+$ ions. The oxygen and carbon contents of specimens were determined using the ^{16}O(d,p$_1$)^{17}O and ^{12}C(d,p$_0$)^{13}C reactions [17,18]. The amounts of oxygen were quantified, to an accuracy of ∼4%, with respect to an anodized tantalum reference specimen of known oxygen content. Carbon was quantified using the average cross-section ratios for the two reactions, with account taken of the energy loss of ^{2}H$^+$ ions in the anodic film [19].

3. Results

3.1. Malonic acid

The voltage–time responses for anodizing aluminium with a 50 nm-thick tungsten-rich tracer layer in malonic and phosphoric acid electrolytes reveal similar linear voltage rises during which the barrier layer and pores develop, followed by a short plateau representing achievement of the major pores characteristic of steady film growth (Fig. 1). After ∼200 s, the voltage again increases due to the first incorporation of tungsten into the film, with peaks occurring at ∼157 and 169 V for the malonic and phosphoric acid electrolytes, respectively. The voltage increment due to incorporation of tungsten species into the anodic film is greater in the malonic acid electrolyte, ∼49 V,
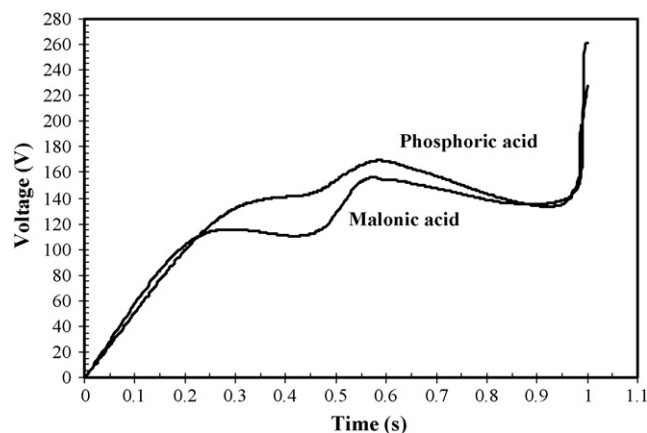

Fig. 1. Voltage–time responses for aluminium, with a 50 nm-thick incorporated tungsten tracer, anodized at 5 mA cm^{-2} in 0.3 M malonic acid and 0.4 M phosphoric acid electrolytes at 293 K. Relative time 1 = 401 and 432 s for malonic and phosphoric acid electrolytes, respectively.