Tracer study of pore initiation in anodic alumina formed in phosphoric acid ☆

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ABSTRACT

Arsenic species are utilized as tracers in a study of pore initiation in anodic films that were formed at constant potentials on aluminium in phosphoric acid. The films were grown first in sodium arsenate solution and then in phosphoric acid, and examined using ion beam analysis and scanning and transmission electron microscopies. The analysis of the arsenic content of specimens indicates that the growth mechanisms of incipient and major pores involve mainly field-assisted dissolution and field-assisted flow of the alumina, respectively. The transition between incipient and major pore formation is suggested to be initiated by preferential growth of certain incipient pores, leading to a locally increased current density at the pore bases. The major pores subsequently develop by the flow oxide away from the pore bases, which is evident from the behaviour of the arsenic tracer. The results suggest that the flow is associated with the non-uniform distribution of ionic current and a relatively low volume of formed film material compared with the volume of oxidized aluminium.

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1. Introduction

Porous anodic alumina films have been of research interest for many years, since they are important for the protection of aluminium alloys against corrosion and wear and provide surfaces suitable for application of paints and adhesives [1–4]. The films have also attracted significant attention for use in nanotechnologies, due to their sub-micron, ordered pores [5–8]. Porous anodic oxides can also be formed on other metals, for example magnesium [9], iron [10,11], tantalum [12], titanium [13–16], tungsten [17] and zirconium [18,19], and the mechanistic understanding of the amorphous alumina films is relevant to these other oxides.

Porous alumina films typically consist of an inner barrier region and a much thicker, outer porous region. The latter contains fine, incipient pores near the film surface, which form soon after the start of anodizing, and larger, approximately cylindrical, major pores, which are present in the main body of film. The major pores develop from a selected number of the incipient pores, with the growth of

other incipient pores then being terminated. It has been suggested that major pores form due to either dissolution of the oxide at the pore bases [20] or flow of oxide [21–23] in the barrier region. Each major pore and the adjacent oxide constitute a cell and, under certain anodizing conditions, cells self-organize as a regular hexagonal pattern [24,25]. The pore diameter, interpore spacing and barrier layer thickness depend on the forming potential, while the thickness of the porous region increases with the charge passed during anodizing. The growth of the films involves the migration of Al^{3+} and O^{2-} ions in the barrier layer [26,27]. Other species, derived from the electrolyte, may also be present in the films, such as phosphate or sulphate ions, with differing migration rates leading to compositional variation in the barrier layer and cell walls [28–31].

Much recent work has been focused on understanding the mechanism of pore formation and the causes of the instabilities that lead to the incipient and major pores [32–40]. Of particular relevance to the present paper, Proost et al. showed that the efficiency of film growth in phosphoric acid changes as pores develop, e.g. from ~0.37 to 0.76 and from a negative value to ~0.1 at current densities of 10 and 1 mA cm^{-2}, respectively [34]. Further, the observation of significant reductions in both the efficiency of film growth and the volume expansion factor (ratio of the thickness of the anodic film to the thickness of oxidized aluminium) with reduction in the current density led to the suggestion that field-assisted dissolution of oxide is a significant factor in the loss of Al^{3+} ions from the films at low current density, while field-assisted ejection

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of Al^{3+} ions dominates as the current density rises [32,33]. Oh and Thompson showed that non-Faradaic, field-assisted dissolution of alumina occurs in films under electric fields of ~8.4 MV cm^{-1} [40]. The films thin uniformly up to a field of ~7.46 MV cm^{-1}, whereas incipient pores form at higher fields, with measurable oxidation of aluminium commencing at ~8.4 MV cm^{-1}. A second instability, involving flow of oxide, leads to later formation of the major pores. It is well established that pore initiation is dependent on topographic features of the aluminium, for example cellular textures on an electropolished surface [37] or impressions produced by a die [6]. Recent studies have considered the possibility that minimization of the mechanical or electrostatic stored energy may lead to instability of a flat alumina surface [35]. Other work has suggested that closely-spaced pores are stable only within a narrow window of anodizing efficiency [38]. Further, the analysis of the effect of viscous flow on the stability of a uniform film subject to periodic deformation has been used to predict pore patterns and pore sizes [39].

In the present study, an ^{18}O-labelled barrier oxide, which contains immobile arsenic species, was grown on aluminium. The aluminium was then re-anodized in phosphoric acid under fields that according to [40] were (i) below the threshold for incipient pore formation, (ii) close to the threshold for commencement of significant oxidation of aluminium and (iii) well above the latter threshold. The arsenic and ^{18}O contents of the films were measured using ion beam analysis, and the pore morphologies and arsenic distributions were studied using scanning and transmission electron microscopies. From these results, the roles of field-assisted dissolution and field-assisted flow in the formation of pores were assessed.

2. Experimental

2.1. Specimen preparation

Specimens of size 30 × 10 mm were cut from 99.99% aluminium sheet that had a cubic texture. They were then electropolished at 20 V for 300 s in a perchloric acid/ethanol mixture (20%:80% by vol.) at 278 K, rinsed in ethanol and then deionized water. After masking with lacquer, an area of ~2 cm^2 was anodized in a two-electrode, glass cell, with an aluminium cathode. The cell contained 30 cm^3 of stirred electrolyte at a temperature of 296 K. The small volume minimized the use of ^{18}O-enriched water. Two sequential anodizing conditions were employed:

(a) a constant current density of 5 mA cm^{-2}, first to 40 V in 0.1 mol dm^{-3} sodium arsenate (pH 9.3, prepared with AR grade $Na_2HAsO_4 \cdot 7H_2O$) and secondly to 100 or 150 V in 0.1 mol dm^{-3} ammonium pentaborate;

(b) first a constant current density of 5 mA cm^{-2} to 60 V in 0.1 mol dm^{-3} sodium arsenate and secondly a constant potential (40, 60 or 110 V—corresponding to the fields (i), (ii) and (ii) mentioned previously) for 15, 60 or 180 s in 0.4 mol dm^{-3} phosphoric acid.

The arsenate electrolyte was prepared using water enriched to ~10% in ^{18}O (CK Gas Products Ltd). Other electrolytes were prepared using deionized water of the natural isotopic composition. Galvanostatic and potentiostatic anodizing used Metronix 6911 and GW DC power supplies, respectively, connected to a data acquisition system (National Instruments) and computer for recording the potential and current responses. Condition (a) was used to determine the mobility of arsenic species in anodic alumina. Condition (b) was used to examine pore initiation during anodizing in phosphoric acid. Following each stage of anodizing, specimens

were rinsed in deionized water. The second stage of anodizing was carried out immediately after the first stage. After completion of anodizing, the specimens were dried in a stream of cool air. For condition (b), a piece was cut from each specimen in order to determine the arsenic and ^{18}O contents of the films formed only in the arsenate electrolyte. After re-masking, the remainder of each specimen was re-anodized in the phosphoric acid. A specimen that had been anodized to 60 V in sodium arsenate electrolyte was also immersed in phosphoric acid for 180 s in order to assess chemical dissolution of the film.

2.2. Specimen examination

Elemental depth profiling of specimens was performed by glow discharge optical emission spectroscopy (GDOES), using a GD-Profiler 2 instrument (Horiba Jobin Yvon). The measurements were made in the continuous mode, using a copper anode of 4 mm diameter, with an argon pressure of 635 Pa and a power of 35 W, and a flush time 30 s. Light emitted by sputtered species was monitored with a sampling interval of 0.01 s at wavelengths (nm) of 396.152 for aluminium, 130.217 for oxygen, 249.678 for boron and 188.980 for arsenic.

Cross-sections of films were prepared by ultramicrotomy for examination by transmission electron microscopy (TEM). The final sections, of ~15 nm nominal thickness, were cut using a diamond knife. TEM employed a JEOL FX 2000 II instrument operated at 120 kV or a FEI Titan G2 80-200 S/TEM instrument operated at 200 kV. The latter was equipped with ChemiSTEM^{TM}, which incorporates four energy-dispersive X-ray (EDX) silicon-drift detectors (SDD). Elemental maps were acquired for 15 min at 256 × 256 pixel resolution, with a pixel size of 1.1 nm. The surfaces of films were observed by scanning electron microscopy (SEM), using a Zeiss Gemini Ultra 55 instrument operated in the range 1 to 3 kV.

Ion beam analyses were carried out using the Van de Graaff accelerator at the Institut des Nano Sciences de Paris. Nuclear reaction analysis (NRA) employed the ^{18}O(p,α)^{15}N and ^{16}O(d,p$_1$)^{17}O reactions, using 750 and 870 keV protons and deuterons, respectively, at normal incidence, with the detector positioned at 150° to the direction of the incident beam. The analyzed area was ~1 mm diameter. A 13 μm-thick Mylar film was placed in front of the detector to stop elastically-scattered particles, thereby providing almost background-free detection. For quantitative analyses, the reaction yields were compared with tantalum oxide references containing $485 \pm 8 \times 10^{15}$ ^{18}O and $690 \pm 20 \times 10^{15}$ ^{16}O atoms cm^{-2}. The accuracies of the ^{16}O and ^{18}O analysis were ~3%. More details of the methods can be found elsewhere [41]. ^{18}O depth profiling was performed using the very narrow resonance of the ^{18}O(p,α)^{15}N reaction at 151 keV. An automatic energy scanning system was used to change the beam energy. A 2 mm diameter beam was incident at 60° to the specimen surface, with an angle of 90° between the beam and the detector. The analyzed area was ~8 mm^2. A 3 μm-thick Mylar film excluded elastically-scattered protons. Details of the method have been published previously [42,43].

Rutherford backscattering spectroscopy (RBS) was carried out using 1.8 MeV He$^+$ ions at normal incidence, with a scattering angle of 165°. The analyzed area was ~1 mm diameter. Data were fitted using SIMNRA software to determine the aluminium contents of the oxides. Arsenic contents (N_{As}) were determined from the yields from arsenic (Y_{As}) in the oxides and from bismuth (Y_{Bi}) implanted into silicon to a known fluence (N_{Bi}—5.55 $\pm$ 0.05 × 10^{15} bismuth atoms cm^{-2}). Rutherford cross-sections were assumed, such that $N_{As} = N_{Bi} (Y_{As}/Y_{Bi}) (Z_{Bi}^2/Z_{As}^2)$, in which Z_{As} and Z_{Bi} are the atomic numbers of arsenic and bismuth, respectively. This method eliminates inaccuracies due to subjectivity in fitting data with simulated spectra. The statistical error in Y_{Bi} was ~1%. The statistical error in Y_{As} for specimens anodized in the arsenate electrolyte was ~5%,