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Role of Oxide Stress in the Initial Growth of Self-Organized Porous Aluminum Oxide

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ABSTRACT

Self-organized porous anodic oxide films are produced when reactive metals such as aluminum and titanium are electrochemically oxidized in baths that dissolve the oxide. The role of oxide stress in the initiation of pores in anodic aluminum oxide was investigated, for constant current anodizing in phosphoric acid. Through-thickness profiles of the in-plane stress in the oxide were measured by in-situ monitoring of stress change during open circuit dissolution following anodizing. During barrier oxide growth prior to pore formation, compressive stress accumulated to several GPa within a 3–5 nm thick layer at the oxide surface, while stress in the interior of the oxide was relaxed. Oxide composition measurements revealed elevated concentrations of incorporated phosphate ions in the same region, indicating that stress is generated by field-driven anion incorporation. Pores initiate when surface stress reaches a maximum, and is accompanied by oxide flow establishing the pore shape. It is suggested that pores are created by a flow instability caused by spatially nonuniform near-surface compressive stress.

1. Introduction

Porous anodic oxide films are formed by electrochemical oxidation of aluminum, titanium and other metals in solutions in which the oxide is soluble. Anodic films produced at particular process conditions contain spontaneously ordered hexagonal arrangements of submicron-diameter cylindrical pores [1]. These self-organized porous anodic oxides have been studied extensively as templates for nanostructured devices and as functional materials [2–4]. For example, much recent work has explored the use of TiO_2 nanotubes in dye-sensitized solar cells, photocatalysis and sensors. Understanding of the oxide growth and metal dissolution processes that control the porous oxide morphology has enabled the improvement of these devices. Further advancements in the design and processing of anodic oxides will be possible by development in models based on mathematical descriptions of these processes [5–8]. Ultimately, models should be able to predict the bath compositions and anodizing voltages in which self-organized oxides are produced, and the scaling relations relating processing conditions to porous layer geometry. The experiments reported here focus on identifying the critical factors that govern pore initiation, so as to guide the development of anodizing models.

During growth of porous anodic oxides, ionic current concentrates at the relatively thin "barrier" oxide layer separating the base of each pore from the metal substrate, while newly formed oxide accumulates in the pore walls. Early explanations for porous layer growth suggested that pores grow by preferential oxide dissolution at the pore base [5,9–11], but later experiments indicated that oxide dissolution rates are in fact very small [12–15]. Recent work has introduced pore formation mechanisms in which oxide stress plays a prominent role. Since anodizing produces compressive stress in the oxide that increases with anodizing current density [16–21], stress should be elevated near the pore base where the current density is high. Thus, stress-driven ionic transport toward the pore walls is envisioned to assist pore formation. Various investigators have suggested transport mechanisms by elastic displacement [22–24], stress-affected ion migration [8], or oxide flow [16,25–28].

Oxide flow during anodizing is supported by a significant body of evidence. Flow in anodic oxides was originally noted by Bradhurst and Leach, in experiments where Al wires were anodized while under tension [29]. They found that elastic stress in preformed anodic films on loaded wires was entirely relaxed

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when ionic current began to flow through the films. Wüthrich observed that anodic alumina films cracked under tensile strain with no applied current, while straining during anodizing produced no cracks [16]. Detailed evidence of oxide flow during Al anodizing was obtained by imaging of tungsten tracers which had been introduced into the metal substrate [26,30]. It was found that the tracers were retained in the formed anodic oxide, rather than dissolving into solution; retention was explained by inward oxide flow opposing outward electrical migration of the W^{+6} ions. Later, the tracer profiles were predicted with quantitative accuracy with a model based on ionic transport by coupled ionic migration and viscous flow [6]. Viscous flow is apparently promoted by the structural disorder and significant free volume in amorphous anodic films, along with the electric field in the oxide during anodizing. Abundant evidence for room temperature viscous flow of other amorphous thin films has been noted in ion irradiation studies [31–34].

While stress generation and flow in anodic films are supported by experimental evidence, the specific role of stress in the formation and self-ordering of pores remains unknown. Recently, we introduced measurements of residual stress distribution in anodic oxides, by monitoring stress changes during controlled open-circuit dissolution of the anodic film immediately following anodizing [21]. Using this method, we found that anodizing produces stress at both the metal-oxide and oxide-solution interfaces. It was shown that compressive stress is produced at either interface when oxide is formed there, and tensile stress is generated at an interface when the oxide "lattice" is destroyed [35]. Typical current densities used in anodizing result in compressive oxide stress and tensile stress at the metal-oxide interface. In the present work, the open-circuit dissolution approach is used to characterize the evolution of stress distributions during the initial stage of conformal barrier oxide growth that directly precedes pore initiation. The measurements reveal that during anodizing, accumulation of elastic compressive stress in the oxide is localized within a layer of a few nanometers thickness close to the oxide-solution interface, while stress in the interior of the oxide is relaxed. We show that pore formation initiates along with oxide flow, when the stress in the near-surface layer builds to a maximum value. It is argued that pores form as a result of a flow-induced morphological instability associated with nonuniform near-surface stress in the oxide.

2. Experimental Section

Monitoring of stress changes in aluminum samples during anodizing and oxide dissolution was accomplished through measurements of sample curvature, by phase-shifting curvature interferometry [36]. A detailed description of the curvature interferometry method, along with validation and comparisons to traditional deflectometry measurements, may be found in an earlier paper [20]. The aluminum samples were rectangular in shape (2.5 × 3.5 cm) and cut from 1 mm thick hard aluminum sheet of 99.998% purity (Alfa Aesar). A reflective gold coating was applied to the opposite side of the sample from that used for anodizing, in order to monitor the curvature change. Sample surfaces were prepared by etching in 10 wt% NaOH for 1 min at 60 °C, followed by immersion in 30 vol% HNO_3 [20,21]. Anodizing was performed at a constant current density of 5 mA/cm^2 in 0.4 M H_3PO_4 at room temperature, using a two-electrode power supply (Keithley 2400) and a platinum wire counter electrode. The anodizing current density was calculated from the applied current and the discolored anodized surface area measured after each experiment.

The measured sample curvature was used to determine the force change per unit width, using the thin-film Stoney approximation,

$$dF_w = \frac{E_s h_s^2}{6(1-\nu_s)} d\kappa \tag{1}$$

where dF_w is the force change per width and $d\kappa$ is the curvature change. h_s,E_s and ν_s are the thickness, elastic modulus and Poisson's ratio of the Al sheet. The force per width F_w represents the biaxial in-plane stress, σ_{xx}, integrated through the sample thickness, relative to that before anodizing,

$$F_w = \int_0^\infty \sigma_{xx} dz \tag{2}$$

where coordinate directions x and z are respectively parallel and perpendicular to the sample surface, and the z axis extends into the metal from its origin on the surface.

Residual stress profiles in anodic oxide films were determined by monitoring curvature changes during open-circuit dissolution immediately following anodizing. Details of this method are found in a previous communication, along with evidence validating the measurement of residual stress profiles [21]. After completion of anodizing, the current was set to zero to dissolve the anodic oxide at open circuit. The oxide thickness as a function of dissolution time was measured by the "re-anodizing" method established in the anodizing literature [37]. That is, the oxide thickness at a selected dissolution time was determined from the initial voltage measured upon re-application of anodizing current. The residual in-plane oxide stress at a particular depth was calculated by numerically differentiating force with respect to thickness, i. e. by dividing the change of force per width by the change in thickness, for the same interval of dissolution time.

Elemental composition depth profiles in anodic oxides were acquired with glow discharge optical emission spectroscopy (GDOES), taking advantage of its high sensitivity and depth resolution in such measurements [38]. A GD-Profiler 2 (Horiba Jobin Yvon), operating in the radio frequency mode at 13.56 MHz was used for depth profiling of the specimens. The profiling was carried out in an argon atmosphere at 700 Pa and 35 W, with a data acquisition time of 0.005 s. The emission lines (nm) used for the analyses were 396.15 for aluminum, 130.21 for oxygen and 178.28 for phosphorus. Scanning electron microscopy observation of the oxide morphology was carried out using a microscope equipped with a field emission gun (FEI Quanta 250).

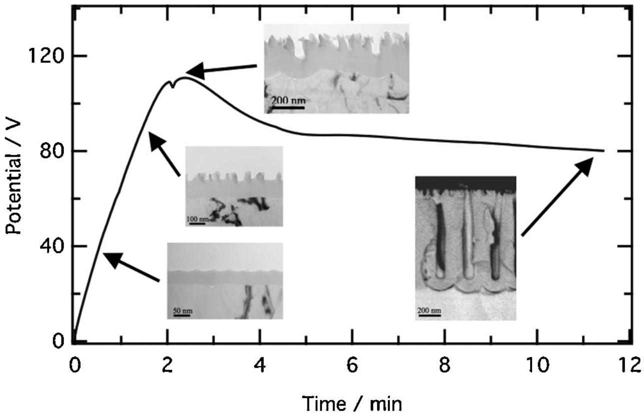

Fig. 1. Potential transient during constant current anodizing of aluminum at 5 mA/cm^2 in 0.4 M H_3PO_4. Images depict cross sections of anodic oxides formed to comparable voltages at 4.5 mA/cm^2, from work by Baron-Wiechec et al. [14].