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Oxide Microstructural Changes Accompanying Pore Formation During Anodic Oxidation of Aluminum

Shinsuke Ide[a], Ömer Özgur Çapraz[a], Pranav Shrotriya[b], Kurt R. Hebert[a,*]

[a] Department of Chemical and Biological Engineering, Iowa State University, Ames, IA 50011, USA
[b] Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA

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ABSTRACT

Porous anodic oxide formation results from a morphological instability of uniform barrier oxide growth leading to the establishment of pores. To gain insight into this process, evidence for microstructural changes in the oxide accompanying pore initiation in anodic alumina was sought through two types of experiments: potentiodynamic anodizing and stress measurements during dissolution of the anodic films. Cyclic voltammetry during anodizing in sulfuric acid shows that pore formation coincides with the appearance of localized ohmic- conducting regions close to the oxide-solution interface of individual pores. These defects induce large current increases which are apparently responsible for growth of concave scalloped features on the metal-oxide interface at the pore base. It is argued that interface defects are generated by surface forces in the oxide that accompany flow contributing to pore initiation. Stress measurements reveal that pore initiation introduces tensile residual stress into the oxide at the pore base, suggesting the formation of vacancy-type defects in the film. Such defects are explained by increases of local conduction current density due to the concentration of anodizing current in pores. Both sets of experiments reveal that pore formation generates locally defective oxide, which may help explain the phenomenon of burning during high-rate anodizing.

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1. Introduction

Porous anodic oxide (PAO) films are produced by electrochemical oxidation of aluminum, titanium and other reactive metals in solutions where metal ions dissolve concurrently during oxidation. Under certain conditions, these films self-organize into arrays of cylindrical nanoscale pores that exhibit hexagonal ordering over macroscopic dimensions. The high degree of order and controllable dimensions of PAO has led to much research into applications such as photoelectrochemical devices, dye-sensitized solar cells, biosensors, metal-ion batteries and supercapacitors [1,2]. Formation of porous films follows an initial stage in which the anodic oxide grows as a barrier layer with planar interfaces [3]. At a critical thickness or voltage, the interfaces of the barrier oxide become unstable, and a pattern of ripples appears at the oxide-solution interface from which the pores emerge.

The mechanism of the transition from barrier to porous oxide is actively debated. Early electron microscopic studies showed that pore formation is accompanied by reduction of the barrier oxide thickness at the base of incipient pores [4]. The prevalent explanations for the local thickness decrease are electric field-assisted oxide dissolution and oxide flow from the pore base toward the pore walls [4–8]. Oxygen isotope studies of aluminum anodizing, though, have revealed no significant oxide dissolution [9–11], even when focused explicitly on the initial formation of pores [12]. The oxide flow mechanism is supported by imaging of implanted tracers demonstrating continuous displacement of oxide from the base to the walls of pores [5,12], and quantitative prediction of these tracer profiles by a simulation of viscous oxide flow during anodizing [6]. It has been proposed that flow is driven by stress induced by volume expansion upon metal oxidation [13,14], electrostatic stress [5,15], or near-surface compressive forces induced by electric field-induced incorporation of electrolyte anions [16–18]. A model for self-ordered porous oxide growth based on the latter mechanism yields promising predictions of the critical conditions for pattern formation [8].

The barrier to porous oxide transition, whether accomplished by flow or dissolution, may produce measureable disturbances to the local oxide microstructure. For example, the onset of flow at pore initiation suggests the presence of significant mechanical forces in the oxide. Such forces in turn may generate detectable defects in the oxide. Here we describe two types of experiments

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that suggest evidence for oxide defects arising from pore initiation. Anodizing of aluminum in sulfuric acid solutions using potentio-dynamic voltage ramps reveals that pore initiation induces large current increases that depends linearly on potential [19]. In the present work we explore the breakdown of oxide conductive resistance implied by these experiments. Modeling the potentio-dynamic anodizing experiments shows that the current increases imply the sudden appearance of localized ohmic-conducting microporous oxide at the solution interface. Further, the formation of defects within the oxide is investigated with in situ stress measurements during open-circuit dissolution of anodic alumina films formed in phosphoric acid. These measurements reveal residual stress in the oxide produced during the barrier to porous oxide transition, thus indicating formation of defects in the film. The relevance of both types of defects in the process of pore formation is discussed.

2. Experimental Methods

Aluminum specimens for cyclic voltammetry were 99.99% 100 μm thick foils (Toyo). Prior to experiments, the foils were degreased with acetone and etched in 10 wt% NaOH followed by a dip in 30 vol% HNO$_3$. Solutions for all experiments were prepared from reagent grade chemicals and deionized water. Cyclic voltammetry (CV) was carried out in aerated aqueous H$_2$SO$_4$ solutions at ambient temperature (close to 23 °C), using a conventional three-electrode cell controlled by a potentiostat (Gamry Reference 3000) with Ag/AgCl reference electrode and Pt wire counter electrode.

In situ stress measurements were carried out using the phase-shifting curvature interferometry method. Al samples for in situ stress measurements were prepared from 1 mm thick 99.998% purity sheet. Details of the procedures of these experiments and representative results are found in other publications [16,18,20,21]. A gold coating applied to on one side of the sample functioned as a reflective surface for interferometry, while the opposite side of the sheet contacted the 0.4 M H$_3$PO$_4$ anodizing bath. Anodizing was at constant applied current density. Changes of sample curvature were monitored using phase-shifting curvature interferometry, during both anodizing itself and subsequently while the anodic oxide dissolved at open circuit. The changes of curvature and force per sample width are related by the thin-film Stoney equation,

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

where dF_w and $d\kappa$ are the force change per width and the curvature change; E_s, h_s and ν_s are the elastic modulus, thickness and Poisson's ratio of the Al sheet. F_w represents the in-plane biaxial stress change integrated through the sample thickness. In the present experiments, F_w is determined primarily by stress in the anodic oxide.

3. Results and Discussion

3.1. Effect of pore initiation on cyclic voltammetry response

The typical cyclic voltammetric response during aluminum anodization in sulfuric acid solutions is illustrated in Fig. 1. Anodic-direction scans exhibit current plateaus extending up to about 2 V. This part of the CV closely resembles galvanostatic anodizing experiments, for which the typical voltage response is a linear increase with time. When the anodic potential limit is less than 2 V, upon scan reversal the current decreases rapidly to values near zero. Similar CV shapes with anodic-direction plateaus are also found during formation of barrier anodic oxide films in neutral
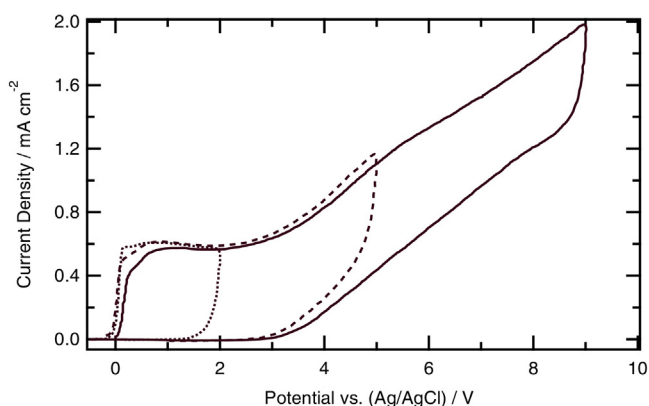

Fig. 1. Effect of anodic potential limit on cyclic voltammetry in 0.4 M H$_2$SO$_4$ at 0.05 V/s. The current is highest during the anodic-direction scan of each cycle.

solutions [19,22–27]. The abrupt decrease of current upon scan reversal is caused by the highly sensitive exponential dependence of current on the electric field in the oxide, according to the high-field conduction law [27].

Fig. 1 shows that when the limiting potential exceeds 2 V, the current density above this "critical" potential breaks away from the plateau, increasing linearly with voltage during both the anodic and cathodic-direction scans. Similar CV shapes were found by Curioni et al. during Al anodizing in sulfuric acid [19]. Curioni reported detailed TEM observations showing that the onset of the linear current increase coincides with the transition from the barrier oxide to the classic porous anodic oxide morphology. They noted continuous increases of the width of individual pores during the anodic-direction scan at potentials higher than the critical value, accompanied by enlargement of scalloped depressions at the metal-oxide interface beneath each pore. They did not explain the linearity of the current-voltage curve. In contrast to Fig. 1, pore initiation during galvanostatic anodizing is accompanied by relaxation of the potential to a steady-state value. The potentio-dynamic experiments therefore extend the potential range of typical anodizing procedures to higher values, and accordingly reveal the current-potential characteristics of pores.

In voltammetry, linear current-potential response over a wide potential range (7 V in Fig. 1) is typically interpreted as a controlling ohmic resistance, especially when the current-potential slope is the same in both scan directions. Fig. 1 therefore suggests that pore formation coincides with the introduction of a large ohmic resistance. The effect of solution ohmic resistance was investigated by varying the acid concentration and thus the conductivity of the anodizing bath. Fig. 2 (a) displays a series of cyclic voltammetry experiments with a constant scan rate of 0.1 V/s using anodizing baths with different H$_2$SO$_4$ concentrations. The slope of the rising anodic-direction current above the critical voltage increases with acid concentration. In addition, the increase of the plateau current density with concentration is consistent with the decrease of current efficiency at lower pH due to a higher rate of Al^{+3} ion dissolution from the oxide surface [27,28]. The decrease of the "critical" potential with acid concentration parallels that of the steady-state anodizing potential [29], and is thus consistent with observations that this potential coincides with pore initiation [19]. As noted in the Introduction, oxygen isotope measurements consistently reveal no significant loss of oxygen ions during anodizing; hence, no enhancement of O^{-2} dissolution at higher concentration should be expected. Neither the reduced current efficiency or lower pore initiation potential at