



Stress induced by incorporation of sulfate ions into aluminum oxide films

Qi Dou^{a,b}, Quentin van Overmeere^{c,1}, Pranav Shrotriya^d, Wenfang Li^b, Kurt R. Hebert^{a,*}

^a Department of Chemical and Biological Engineering, Iowa State University, Ames, IA 50014, United States

^b School of Materials Science and Engineering, South China University of Technology, Guangzhou, 510641, China

^c Institute of Mechanics, Materials and Civil Engineering, Université catholique de Louvain, Louvain-la-Neuve B-1348, Belgium

^d Department of Mechanical Engineering, Iowa State University, Ames, IA 50014, United States



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ABSTRACT

The geometry of self-ordered porous anodic aluminum oxide films depends strongly on the type of acid anion in the anodizing solution. Recent studies suggest that electric field-induced anion incorporation in the oxide may generate compressive surface stress that drives oxide flow responsible for formation of self-ordered arrays of pores. This communication reports direct evidence for sulfate ion incorporation-induced compressive stress in native aluminum oxide films from stress measurements during open-circuit Al dissolution in 0.4 M H₂SO₄, coupled with analysis of the film composition by X-ray photoelectron spectroscopy. The measured force per width (integrated in-plane stress) was compared to the calculated elastic force assuming that all detected sulfate ions are incorporated in the oxide, rather than adsorbed on the oxide surface. Quantitative agreement was demonstrated between the calculated and experimental force, showing that sulfate incorporation dominates over adsorption and induces greater than 1 GPa levels of compressive stress in the oxide. The present work and an earlier study of phosphate incorporation show that anions incorporate at small open-circuit exposure times, when the outer portion of the oxide can support a high electric field because it is not yet completely hydrated. Therefore the electric field in the oxide is the likely driving force for incorporation.

1. Introduction

Incorporation of electrolyte anions in anodic aluminum oxide films is thought to play a key role in the formation of self-ordered porous anodic films. The pore diameter and spacing between pores depend sensitively on the type of acid used as the anodizing bath, such as sulfuric, phosphoric or oxalic acid. These anions incorporate in the oxide and strongly influence ionic migration kinetics [1–4]. Recent evidence indicates that anodic alumina flows at the high electric fields present during anodizing, and that formation and self-ordering of pores results from a flow instability [5–8]. We proposed that the driving force for this flow is elevated localized compressive stress in the oxide that was detected close to the oxide-solution interface [7,9,10]. The stress may originate from electric field-stimulated incorporation of oxygen and acid anions, since high concentrations of such anions are found in the compressively-stressed layer; incorporation may then explain the strong influence of anions on anodizing. However, to properly evaluate the flow instability model, direct evidence should be obtained that anion incorporation can induce surface stress. Anion incorporation in oxide layers also has broader significance in areas other than anodizing.

For example, competitive incorporation of aggressive (e.g. Cl⁻) and inhibiting oxyanions in surface oxide films on metals such as aluminum, iron, nickel and their alloys results in localized passivity breakdown, leading to pitting and crevice corrosion [11,12].

In situ stress measurements can be used to experimentally probe time-dependent anion incorporation in electrochemical experiments. Absorption of oxyanions such as sulfate, phosphate and oxalate produces volume expansion. Since the oxide layer is attached to a rigid metal substrate, expansion occurs only in the out-of-plane direction, and biaxial compressive stress is generated parallel to the surface. In-plane stress is equilibrated by substrate curvature changes which are measured to determine the stress. Stress measurements are highly sensitive because of the large elastic moduli of metals and the availability of high-resolution curvature measurement techniques. For example, stress changes have been used to monitor hydrogen absorption and vacancy injection during Al corrosion [13,14]. The present communication reports a study of anion incorporation-induced stress in the native oxide layer on aluminum during open-circuit dissolution in sulfuric acid. Accumulation of SO₄⁻² ions is measured with X-ray photoelectron spectroscopy (XPS), which detects both adsorbed and

* Corresponding author.

E-mail address: krhebert@iastate.edu (K.R. Hebert).

¹ Present address: Palo Alto Research Center, Palo Alto, CA 94304, United States.

absorbed (incorporated) anions. The elastic stress assuming hypothetically that all detected anions are incorporated is then compared to in situ stress measurements during dissolution, to elucidate the relative contributions of adsorption and incorporation. The present results together with those of our recent study of phosphate incorporation provide direct evidence of electric field-induced oxyanion incorporation in aluminum oxide films [10].

2. Experimental details

Aluminum samples were rectangular coupons (2.5×3.5 cm) cut from 1 mm thick 99.998% purity sheets (Alfa Aesar). The sample surfaces were pretreated by cleaning with acetone and deionized water, followed by etching in 10 wt% NaOH for 1 min at 60°C and finally immersion in 30 vol% HNO_3 for 30 s. Corrosion tests consisted of open-circuit exposure of the Al sample in aqueous 0.4 M H_2SO_4 solution for specified times. Potential measurements used a Ag/AgCl reference electrode and a potentiostat (Gamry Reference 3000). In situ stress measurements employed the phase shifting curvature interferometry method [15]. The applications of this technique to anodic oxidation and open-circuit corrosion experiments were described in earlier publications [7,9,14,16,17]. One side of the Al sample was mechanically polished to serve as a reflective surface for interferometry. The specimen was mounted in a test cell with the unpolished side in contact with the electrolyte solution and the opposite side facing the optical system. Changes in sample curvature during dissolution or anodizing were monitored [14,16]. The curvature change ($d\kappa$) is related to the near-surface force per width (dF_w) according to the Stoney thin-film approximation,

$$dF_w = \frac{E_S h_S^2}{6(1 - \nu_S)} d\kappa \quad (1)$$

where E_S , ν_S and h_S are respectively the elastic modulus, Poisson's ratio and thickness of the Al sample. The force per width is the in-plane biaxial stress σ_{xx} integrated through the sample thickness,

$$F_w = \int_0^\infty \sigma_{xx} dz \quad (2)$$

where the x axis is parallel to the Al surface, and the z axis extends toward the bulk metal from its origin at the surface. Force per width is referenced to the initial state of the sample before immersion in acid, and compressive and tensile force changes are respectively negative and positive in sign.

After dissolution treatments, samples for XPS analysis were rinsed with distilled and deionized water and then dried under an air stream. Measurements were carried out using a K-alpha instrument (Thermo Scientific). The binding energy scale of the instrument was calibrated with sputter-cleaned Cu and Au. The transmission function of the analyzer is approximated by a cubic relationship between the logarithm of peak intensity, normalized by sensitivity and pass energy, and the logarithm of the retarding ratio. The pressure in the XPS chamber was always lower than 8×10^{-8} Pa.

3. Results and discussion

XPS spectra of Al samples after dissolution in 0.4 M H_2SO_4 included peaks from aluminum, oxygen, sulfur and carbon contaminant. Relative concentrations of film species were inferred from the areas of the S 1s, O 1s, and Al 2p peaks. The S signal derives from both adsorbed SO_4^{2-} ions on the oxide surface and incorporated (adsorbed) sulfate ions within the oxide. Deconvolution of the Al 2p peak resolved its area into contributions from Al ions in the oxide (Al_{ox}) and Al atoms in the metal (Al_{met}). Fig. 1(a) shows the dependence of the concentration ratios S/Al_{ox} and $\text{O}/\text{Al}_{\text{ox}}$ on open circuit exposure time in 0.4 M H_2SO_4 . The $\text{O}/\text{Al}_{\text{ox}}$ ratio was 1.56 ± 0.1 , indicating that the overall film composition

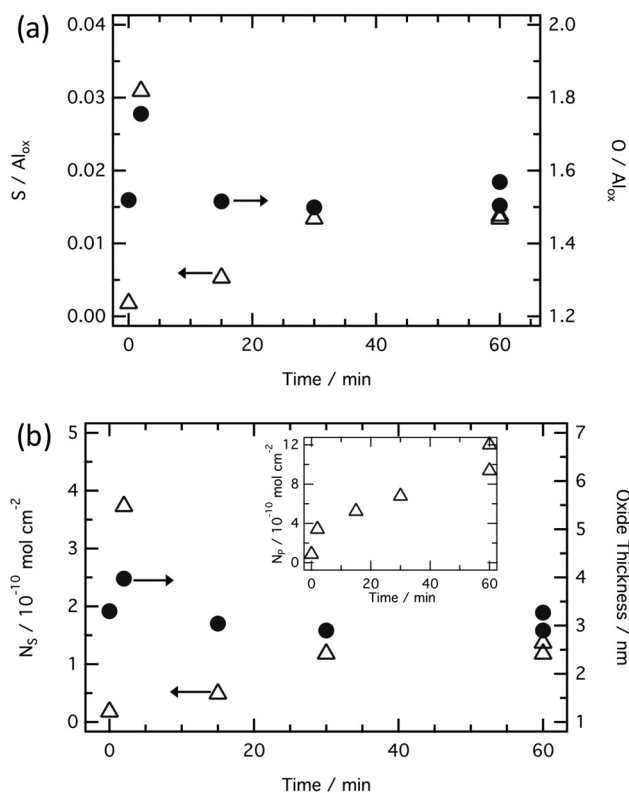


Fig. 1. XPS measurements of thickness and composition of the native oxide film on Al after open-circuit dissolution in 0.4 M H_2SO_4 . (a) Relative concentrations of S and O vs. Al in the oxide. (b) S concentration per unit area and oxide thickness. The inset shows the P concentration after dissolution in 0.4 M H_3PO_4 [10].

remained close to Al_2O_3 . The S/Al_{ox} ratio exhibited a non-monotonic time dependence: S/Al_{ox} increased sharply to 0.031 at 2 min, and thereafter decreased to values between 0.005 and 0.014 at times of 15 to 60 min. The thickness of the oxide layer was calculated from the relative areas of Al_{ox} and Al_{met} (Fig. 1(b)) [18]. The oxide was found to be 3.2 ± 0.4 nm thick, with a somewhat larger apparent thickness at 2 min. Fig. 1 (b) also displays the S concentration N_S , which was determined from the oxide thickness and S/Al_{ox} from Fig. 1 (a). N_S represents the sulfate concentration per area, and includes adsorbed ions as well as adsorbed ions distributed through the entire oxide thickness. The S concentration exhibits the same non-monotonic time dependence as the S/Al_{ox} ratio, with a pronounced maximum concentration at 2 min.

The inset in Fig. 1(b) shows the P concentration per area in the surface oxide (N_P), measured by XPS after various open-circuit exposure times in 0.4 M H_3PO_4 [10]. Similarly to N_S , N_P derives from adsorbed and incorporated PO_4^{3-} ions. Both N_S and N_P abruptly increase in the initial 2 min to concentrations close to $4 \times 10^{-10} \text{ mol/cm}^2$. However, at later times when N_S decreases, N_P continues to increase at a reduced rate relative to the first 2 min of exposure. At 60 min, the PO_4^{3-} concentration is about ten times higher than that of SO_4^{2-} . The trends suggest that a common process controls accumulation of both anions in the first 2 min, but at later times adsorption or incorporation kinetics differ according to the anion type.

Force per width transients during open-circuit dissolution in 0.4 M H_2SO_4 are shown in Fig. 2(a). The force changed rapidly in the compressive (negative) direction to a minimum of -5 N/m at 2 min, and then increased abruptly between 2 and 15 min. After 15 min, the force remained between -2 and 0 N/m for times up to 60 min. The maximum average stress in the oxide from the measured thickness is about -1.5 GPa . The contribution of anion incorporation to the measured force was evaluated by calculating the elastic force implied by the XPS

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