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Measurement of Stress Changes during Growth and Dissolution of Anodic Oxide Films on Aluminum

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While stress is thought to play an important role in the development of self-organized porous films, mechanisms of stress generation during anodizing are not yet understood. In order to reveal depth distributions of stress in anodic films, phase-shifting curvature interferometry was used to monitor force transients (in-plane stress integrated through the sample thickness) during formation of anodic oxides on aluminum in phosphoric acid, as well as subsequent open-circuit dissolution. The measurements were not influenced significantly by electrostatic stress, internal stress in the metal samples, thermal stress, or stress induced by open-circuit dissolution. At typical current densities, the force became more compressive during anodizing, while a net tensile force change was measured after anodizing followed by complete oxide dissolution. Thus, it was revealed that anodizing generates both compressive stress in the oxide and tensile stress near the metal-oxide interface. Analysis of the open-circuit stress change revealed separate contributions from diffusional stress relaxations, and removal of residual oxide stress by dissolution. Residual stress distributions in the oxide, at nanometer depth resolution, were determined from measurements of dissolution rate and stress at open circuit, and validated through variations of the open-circuit dissolution rate.

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Porous anodic oxide films are formed by electrochemical oxidation of selected metals, such as Al, Ti, and Zr, in baths which dissolve the oxide.1–7 For particular applied voltage and solution composition, anodizing produces self-organized arrays of cylindrical pores tens to hundreds of nanometers in diameter. The high regularity of the pore distributions, and the ability to adjust the geometry of the porous layers by changing process variables has led to extensive exploitation of these films for diverse applications including solar cells, nanowires and photocatalysts.4 Upon application of the anodizing current or potential, the oxide grows at first as a conformal barrier layer, but at a certain thickness the oxide-solution interface becomes unstable, after which pores are initiated by further oxide growth. Recent studies have provided insight into the reactions and transport processes contributing to anodic oxide growth, and the anodizing conditions that produce ordered porous films.5,6 However, important aspects of porous oxide formation are unexplained, including the mechanisms of the initial instability of the barrier oxide and subsequent pore formation.

The main driving force for anodic oxide growth is an electric field of order 1 V/nm in the oxide, which induces migration of metal and oxygen ions. However, large stress changes also accompany anodizing,7 and are thought to play an important role in film morphology evolution.8–10 Stress gradients can influence mass transport by contributing to the chemical potential gradient driving force for ionic migration, and by inducing viscous flow of oxide.5,6 Despite the acknowledged significance of stress, there is disagreement as to the nature of stress generation processes. Several different stress generating mechanisms have been suggested in prior studies: compressive stress accompanying volume expansion upon conversion of metal to oxide;8 electrostatic stress (i.e. Maxwell stress and electrostriction) due to the electric field in the oxide;11,12 hydration and dehydration of the film;13,14 and formation or annihilation of vacancy defects at the metal interface.15,16 Compressive (tensile) stress may also be produced by insertion (removal) of oxygen ions or electrolyte anions into the amorphous oxide at the solution interface, in analogy to stress generation by metal atom insertion at grain boundaries during thin film growth.17 Additional processes at the metal-oxide interface can contribute to stress changes during anodizing, including removal of residual stress by consumption of metal,18 and transfer of metal atoms between interface ledges and near-surface dislocations.19

Previous experimental studies of anodizing-induced stress have exclusively focused on stress evolution during film growth. Generally, the curvature of thin metal samples attached to inert substrates is monitored, and the average in-plane stress in the surface oxide is deduced from the measured curvature change through use of the Stoney thin-film approximation.20 Several papers have reported conflicting trends on the dependence of stress evolution on current density and solution composition.7,13,15,16,21 Two recent studies, though, used different high-resolution in situ techniques to obtain closely similar stress measurements during growth of barrier oxides on Al in phosphoric acid.22,23 Both papers found increasingly compressive growth stress with increasing current density, in agreement with earlier work by Wüthrich.7 However, measurements of average stress may not provide sufficient information to discriminate among the multiple potential stress mechanisms during anodizing. In studies of growth of thin metal films, stress measurements during growth interruptions and etching of the films have helped identify stress relaxation mechanisms and through-thickness residual stress distributions.17,24–26 Knowledge of such distributions in anodic films would help reveal separate stress-generating mechanisms at the metal and solution interfaces. In the present work, we extend growth interruption measurements to anodic oxidation, by monitoring stress changes during both anodizing at constant applied current, as well as subsequent open circuit dissolution of the oxide. These experiments provide direct information about several stress-generating mechanisms pertinent to anodizing.

Experimental

The aluminum samples used for stress measurement experiments were fabricated from 1 mm thick hard aluminum sheet of 99.998% purity (Alfa Aesar). The yield stress of the sheet was estimated as 89 MPa based on Vickers hardness measurement (Wilson Tukon Hardness Tester). Samples were cut into a rectangular shape (2.5 \times 3.5 cm) using a low speed saw (Buehler Isomet). A reflective gold coating was applied to the opposite side of the sample from that used for anodizing. The Al surface to be anodized was mechanically polished and degreased in acetone, followed by rinsing in deionized water and drying in an air stream. The Al surfaces were then etched in 10 wt% NaOH for 60 s at 60 °C, and then immersed in 30 vol% HNO3 to remove corrosion products.
When these surface preparation procedures were used, the transient voltage response during anodizing was found to be reproducible and consistent with the literature.  

In situ stress measurements were carried out using phase-shifting curvature interferometry. This technique uses interferometry to measure the surface curvature of the metal sample resulting from in-plane near-surface stress induced by anodizing. The present curvature interferometry system and its application to anodizing are fully described in a separate article. During anodizing, two laser beams are reflected twice each from the gold-coated surface on the back side of a sample, while the front side contacts the anodizing solution. The beams accumulate a path length difference when the sample curvature is nonzero. After reflection, the beams are brought together, and the path length difference is determined from the measured intensity of the interfered beam. The path length difference is related to the curvature, and the in-plane stress is calculated from the curvature using the thin-film Stoney approximation,

\[
F = \frac{E_s h^2}{6(1 - \nu_s)} \kappa
\]

where \( \kappa \) is the curvature change; \( h \), \( E_s \), and \( \nu_s \) are the thickness, elastic modulus and Poisson’s ratio of the Al sheet. The force per width \( F \) represents the biaxial in-plane stress \( \sigma_{xx} \), integrated through the sample thickness, relative to that before anodizing:

\[
F = \int_0^\infty \sigma_{xx} dz
\]

where coordinate directions \( x \) and \( z \) are respectively parallel and perpendicular to the sample surface, and the \( z \) axis extends into the metal. The important advantages of the interferometry system include phase-shifting of the reflected beams, which increases measurement sensitivity, and separation of the optical path from the electrochemical cell, which enhances stability. The optical arrangement of the curvature interferometer ensures that the beams are reflected from the same locations on the sample surface during the curvature measurement. Phase shifting interferometry allows direct determination of path length change for beam reflected from the gold surface and enables the high-resolution measurement of curvature change. Curvature changes as small as \( 10^{-3} \) rad can be detected, an order of magnitude smaller than the resolution of state-of-the-art multiple optical beam deflectometry methods.  

Anodizing at constant applied current density was performed in 0.4 M H₃PO₄ at room temperature, using a two-electrode power supply (Keithley 2400) and a platinum wire counter electrode. The liquid volume in the cell was 70 mL. The surface area in contact with the cell was defined by sealant applied around sample perimeter, and was not precisely known prior to experiments. The applied current density was calculated from the discolored anodized surface area measured after each experiment. For the experiments described here, the true applied current density varied by \( \pm 0.2 \) mA/cm² from the nominal value of 5.0 mA/cm². After completion of anodizing, the current was set to zero while continuing to monitor stress as the anodic film dissolved on open circuit. In some experiments, the open circuit dissolution rate was increased by adding concentrated phosphoric acid to the cell upon completion of anodizing, in order to bring the overall H₃PO₄ concentration in the cell to 1.0 M. The open-circuit dissolution rate of the oxide was measured separately from the stress monitoring experiments, using the re-anodizing technique: after a given dissolution time the anodizing current was reapplied, and the remaining oxide thickness determined from the immediate increase in voltage. Re-anodizing has previously been shown to yield reliable anodic oxide thickness measurements. Additional potentiodynamic experiments were performed to identify the onset potential of anodizing, using a high-voltage potentiostat (Gamry Reference 3000). The scan rate was selected to be the same as the rate of potential increase during galvanostatic anodizing. Finally, in order to assess the importance of thermal expansion stress during the present measurements, the Al temperature was measured during anodizing in the stress measurement cell. Temperature was monitored using a thermocouple (Omega K-type) attached to the Al sample.

**Results and Discussion**

*Force transients during anodizing followed by open-circuit oxide dissolution.*— An example of potential and stress measurements during an anodizing experiment is shown in Fig. 1. The aluminum sample was anodized at 4.5 mA/cm² up to 25 V, at which point the current was set to zero while stress monitoring continued during open-circuit dissolution of the anodic film. The force per width plotted in Fig. 1 and elsewhere in this paper is the quantity \( F \) defined in Eq. 2, i.e. the biaxial in-plane stress integrated through the sample thickness. The potential and stress transients can be compared with previous measurements at similar conditions. During the anodizing period, the cell potential increased at a rate of 0.82 V/s. Assuming an oxide density of 3.1 g/cm³ and an electric field of 0.91 V/nm in the barrier film, the film growth rate and oxide formation efficiency are estimated to be 0.90 nm/s and 0.35, respectively. The latter value compares favorably with a directly measured efficiency of 0.33 during anodizing at the same conditions. Based on the oxide thickness and measured force per width at 25 V, the apparent average stress in the oxide at the completion of anodizing was \(-58 \) MPa, in good agreement with prior measurements. Indeed, close agreement with the deflectometry measurements of Van Overmeere et al. was demonstrated over a wide range of current densities during anodizing in phosphoric acid.  

The current interruption was immediately followed by a nearly discontinuous increase of stress in the tensile direction. Fig. 2 is a graph of the force per width measurement from Fig. 1, with magnified time scale near the time of the current interruption at 26.1 s. The slope changes at 28 and 100 s suggest that different stress relaxation processes dominate in the periods 26–28 s, 28–100 s and after 100 s.
closer view of the stress measurement of Fig. 1 around the time of the interruption. Upon interruption, the force per width increased abruptly from $-1.60$ to $-1.40$ N/m in 0.6 s, and thereafter more slowly. The initial rapid tensile force change may be attributable to removal of compressive electrostatic stress, which should relax when the anodizing electric field is removed upon current interruption. The electrostatic stress calculated from the measured force change and the oxide thickness of 27 nm is $-6.2$ MPa. This value is appreciably smaller than $-43$ MPa, the electrostriction stress found by Wüthrich at a comparable electric field. Since the ability of the curvature interferometry system to capture rapid force per width changes has not been independently established, the accuracy of our measurement may be uncertain. Both measurements can be compared to the theoretical contribution to electrostatic stress from Maxwell stress, which is estimated as $-9.3$ MPa, close to our measured value, using a Poisson’s ratio of 0.22 and a relative permittivity of 9 for alumina. However, this comparison is tentative, because the dielectrostriction stress contribution to the electrostatic stress has also been shown to be significant for other anodic oxides. In any case, the electrostatic force was much smaller than the open circuit force change at times of minutes to hours, which is of primary interest in this work.

Following relaxation of the electrostriction stress, Fig. 2 shows that the force per width increased to $-0.62$ N/m at 100 s, and afterwards increased at a distinctly smaller rate. The rate of force change at long times decreased slowly while the anodic film dissolved (Fig. 1). Based on oxide thickness measurements described below, complete dissolution would be expected at 80 min. It is noteworthy that a tensile force value, relative to the reference value of zero before anodizing, is approached in Fig. 1 while oxide dissolution is nearing completion. This illustrates the general observation in this work that anodizing followed by anodic film dissolution produces a significant stress change in the metal sample.

Consideration of possible measurement artifacts.— We now discuss possible artifacts that can influence the experiments, in order to show that the open-circuit force per width transients are directly relevant to anodizing itself. The following paragraphs discuss potential artifacts arising from dissolution-induced stress, internal stress in the metal samples, and thermal stress.

If the force measurements are to be interpreted in terms of anodizing-induced stress, the stress introduced during oxide dissolution should not be significant. The main panel in Fig. 3 shows the force per width change during complete open-circuit dissolution of films grown to 20 V at various current densities, as well as the overall force change during anodizing and open-circuit dissolution in the same experiments. The difference between these values is the force change due to anodizing itself; while the anodizing force is relatively small, it increases reproducibly with current density, as we showed earlier. The clear dependence of both force changes on current density demonstrates that the force per width transients are primarily determined by the anodizing conditions. Therefore, the measured open-circuit force per width change results from stress introduced into the sample during anodizing, and not during the open-circuit period. We reserve discussion of the mechanistic implications of the current density dependence for a later publication.

Experiments with thin-film metal substrates have shown that removal of near-surface internal stress in the metal by oxidation can contribute to the measured stress change during anodizing. In order to assess the significance of internal stress effects in the present measurements, we compared force per width measurements at various applied current densities and formation voltage, under the assumption that the force change due to anodizing followed by complete oxide dissolution is only due to removal of hypothetical metal stress. Accordingly, the inset in Fig. 3 shows the hypothetical internal metal stress, $-\Delta F_{tot}/h_{met}$, where $\Delta F_{tot}$ is the overall force change for anodizing and dissolution, and $h_{met}$ the oxidized metal thickness, obtained from the anodizing charge using Faraday’s law. Results are shown for anodizing at 5 mA/cm² to various potentials, and for anodic films grown to 20 V at different current densities. The figure shows no consistent trend of the calculated stress with oxidized metal thickness; indeed, for the same range of $h_{met}$, the stress from 20 V experiments is much larger than that from the 5 mA/cm² experiment. Since the overall force per width change due to anodizing and dissolution does not depend on $h_{met}$, the figure contradicts the hypothesis that removal of internal metal stress significantly affects the overall force change. Also, the hypothetical stress at 20 V is much larger than the yield stress of the Al samples, which was found to be 89 MPa. Therefore, we conclude that the internal stress in the present sheet samples is not large enough to significantly affect the measured force change. In fact, this was already apparent from the close agreement between the anodizing stress measured using sheet and thin film samples, the latter of which had been corrected for internal stress.

For some anodizing conditions, significant temperature increases caused by Joule heating of the oxide have been observed. Measurements of the aluminum substrate temperature during anodizing were carried out to assess whether thermal effects on the present stress measurements might be significant. Fig. 4 shows the transient variation of the Al temperature and force for anodizing at 7 mA/cm². During anodizing, the temperature increased above the bath temperature by about 1.4 °C, and after switching off the power supply relaxed to its initial value over a period of about 100 s. Thermal mismatch strain is developed due to difference in the coefficient of thermal expansion between the oxide film and the substrate. Since the substrate is

![Figure 3](image1.png)

**Figure 3.** Effect of current density on the components of the force per width change during anodizing to 20 V. Open symbols are the overall force per width change due to both anodizing and open-circuit oxide dissolution; filled symbols are the force per width change during dissolution alone. The inset shows the calculated apparent internal stress in the oxidized metal layer, assuming that the measured overall force per width change is due to removal of internal stress. Experiments involved anodizing to 20 V at various current densities (open symbols), and anodizing at 5 mA/cm² to various potentials (closed symbols).

![Figure 4](image2.png)

**Figure 4.** Temperature of Al substrate measured while anodizing at 7 mA/cm² for 23.6 s, and during subsequent open-circuit period. Force per width measured during anodizing is also shown.
much thicker than the oxide film and there is strong bonding between film and substrate, all the mismatch strain will be applied to the film. Aluminum oxide and aluminum are isotropic materials, so force per width, $F_{th}$, in the film due to thermal expansion mismatch can be estimated as

$$F_{th} = -E_{ox} (\alpha_{ox} - \alpha_{Al}) h_{ox} \Delta T$$

where $\alpha_{ox}$ and $\alpha_{Al}$ are the thermal expansion coefficients of the oxide film and aluminum substrate, with the values of 5 and $23 \times 10^{-6} \text{ K}^{-1}$, respectively. Young’s modulus of the barrier anodic film, $E_{ox}$, is about 120 GPa and the maximum thickness of the film $h_{ox}$ is 40 nm.\(^{3,5,37}\) Hence, based on the measured temperature increase the maximum force per width generated due to thermal expansion mismatch during anodizing may be estimated as 0.10 N/m. As this value is much smaller than the measured force, it is evident that for the present anodizing conditions, thermal mismatch stress is not significant.

Effect of oxide dissolution rate on open-circuit force measurements.— As discussed in the Introduction, two types of processes may contribute to the open circuit force per width change during dissolution: removal of residual stress in the anodic film by oxide dissolution, and relaxation of stress by diffusion of defects to surfaces. While the dissolved oxide thickness determines the extent of residual stress removal, the elapsed time on open circuit should control the progress of diffusional stress relaxation. To discriminate between these mechanisms, we performed stress measurements in which the same anodic film was dissolved at different rates. Examples of two experiments showing the effect of oxide dissolution rate on open-circuit force per width evolution are displayed in Figs. 5 and 6, for anodic films formed to 20 and 40 V, respectively, at 5 mA/cm$^2$ in 0.4 M H$_3$PO$_4$. Each figure shows the force measured during open-circuit dissolution both in the anodizing solution and in 1 M H$_3$PO$_4$. The latter measurements were carried out by adding concentrated phosphoric acid to the cell upon completion of anodizing. The force in 1 M H$_3$PO$_4$ could not be captured within 20 s after current interruption, because of disturbances accompanying solution addition to the cell. The arrows denote the times of complete dissolution of the anodic films, according to measurements of oxide thickness discussed below. In both figures, the force levels before and after oxide dissolution are approximately the same in the two solutions, indicating that the more concentrated acid the same force change was measured over a smaller time period. This would be expected if the overall force change during dissolution is determined mainly by removal of residual oxide stress.

Effect of dissolution rate on open-circuit force per width evolution during open-circuit dissolution of 20 V anodic film. Anodizing was in 0.4 M H$_3$PO$_4$, followed by open-circuit dissolution in either 0.4 M or 1 M H$_3$PO$_4$. The anodizing current densities were 5.0 mA/cm$^2$ (0.4 M) and 4.8 mA/cm$^2$ (1 M). The plotted force per width is relative to the aluminum sample before anodizing, and therefore includes the compressive force per width induced by anodizing ($\sim -3.15$ and $-2.67$ N/m for the 0.4 and 1 M experiments, respectively). Arrows mark the times of complete dissolution of the oxide, at 128 and 92 min in the 0.4 M and 1 M solutions, respectively.

In general, the open circuit dissolution measurements exhibited a distinctly faster force per width change in the first minute of the open circuit period. The sign and magnitude of this early force change depended on both anodizing current density and potential. In Figs. 1, 5 and 6, the force per width changed by 0.7, $-0.9$ and 0.9 N/m during time intervals of 60, 40 and 50 s after the electrostatic stress relaxation. In Figs. 5 and 6, both the 0.4 and 1.0 M H$_3$PO$_4$ force per width transients had nearly the same time dependence during the first minute on open circuit. This suggests that the initial portions of the force transients may be controlled by a time-dependent diffusional relaxation, as opposed to removal of residual stress by oxide dissolution. In contrast, the overall rate of force change over the entire dissolution period is clearly larger in the more concentrated solutions, in which more rapid dissolution is expected.

Depth distributions of residual oxide stress.— The interpretation of open circuit force evolution in terms of stress relaxation at small time scales of $\sim$ 1 min, and residual stress removal on longer time scales, was tested by quantitative analysis of the oxide dissolution experiments. Oxide thickness changes during dissolution were measured using re-anodizing experiments, and used to calculate residual stress distributions from the force transients in Figs. 5 and 6. Comparison of stress distributions obtained at each phosphoric acid concentration then helped evaluate to what extent force evolution was controlled by residual stress removal. In broader terms, the results in this section validate our approach to determine residual stress distributions in anodic oxides. Analysis of these distributions can reveal separate stress-generating processes at the metal and solution interfaces.

Figure 5. Effect of dissolution rate on force per width evolution during open-circuit dissolution of 20 V anodic film. Anodizing was in 0.4 M H$_3$PO$_4$, followed by open-circuit dissolution in either 0.4 M or 1 M H$_3$PO$_4$. The anodizing current densities were 5.3 mA/cm$^2$ (0.4 M) and 4.7 mA/cm$^2$ (1 M). The plotted force per width is relative to the aluminum sample before anodizing, and therefore includes the compressive force per width induced by anodizing ($\sim -1.35$ and $-1.19$ for the 0.4 and 1 M experiments, respectively). Arrows mark the times of complete dissolution of the oxide, at 74 and 52 min in the 0.4 M and 1 M solutions, respectively.

Figure 6. Effect of dissolution rate on force per width evolution during open-circuit dissolution of 40 V anodic film. Anodizing was in 0.4 M H$_3$PO$_4$, followed by open-circuit dissolution in either 0.4 M or 1 M H$_3$PO$_4$. The anodizing current densities were 5.0 mA/cm$^2$ (0.4 M) and 4.8 mA/cm$^2$ (1 M). The plotted force per width is relative to the aluminum sample before anodizing, and therefore includes the compressive force per width induced by anodizing ($\sim -3.15$ and $-2.67$ N/m for the 0.4 and 1 M experiments, respectively). Arrows mark the times of complete dissolution of the oxide, at 128 and 92 min in the 0.4 M and 1 M solutions, respectively.

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Figure 7 shows examples of potential transients during re-anodizing following partial dissolution of an anodic film formed to 20 V. After the indicated times at open circuit, the original anodizing current density was reapplied; the resulting potential transients are shown in the figure. The measured anodizing potential is related linearly to the oxide thickness, according to the electric field of 0.89 V/nm at this current density.\(^{29}\) In each transient, the potential increased abruptly to a value establishing the electric field needed to drive anodizing current through the remaining barrier oxide. Subsequently, the potential increased at a constant rate, indicating uniform barrier oxide growth.\(^{29}\) In Fig. 7, the potential of uniform oxide growth is reached immediately after 5, 10 and 90 min open circuit dissolution, and at 0.7 s after dissolution for 20 and 55 min. The decreasing re-anodizing potential with dissolution time is expected due to the smaller remaining oxide thickness after partial dissolution.
For each dissolution time, the barrier oxide thickness was calculated from the potential at the initiation of uniform oxide growth during re-anodizing. The re-anodizing potential was converted to thickness using the above-mentioned electric field. The potential at the metal-oxide interface was taken to be 0.0 V, the onset potential of the anodizing current wave observed during potentiodynamic polarization of Al in 0.4 M H₃PO₄. Fig. 8 shows the resulting dependence of the oxide thickness on time during dissolution in 0.4 M or 1.0 M H₃PO₄. The final thicknesses of 3 nm in both experiments represent a limiting oxide thickness that could not be reduced by further dissolution; when this thickness is reached, the metal begins to dissolve while the oxide thickness remains constant. Fig. 8 shows that the open circuit dissolution time in 1.0 M H₃PO₄ was 30% smaller than that in the 0.4 M solution. The relative dissolution rates compare favorably to the force transients in Fig. 5, in which the time to reach the maximum force was 29% smaller in the 1 M solution. The similar time dependences of the force and oxide thickness again indicates that removal of residual oxide stress controls the force transients at times of 10–100 min. For both phosphoric acid solutions, the oxide thickness data were well approximated by two linear time dependences, with the outer layer of the oxide apparently dissolving at a higher constant rate compared to the inner portion. Several reports in the literature have found similarly enhanced dissolution in the outer layer, which has been explained by effects due to incorporated electrolyte anions.

Based on the oxide thickness measurements, hypothetical residual stress distributions were calculated from the force evolution results in Figs. 5 and 6. Using the oxide thickness measurements, time intervals were identified corresponding to 1 nm increments of oxide dissolution. The force per width change over each such interval was divided by 1 nm to obtain the average in-plane stress within the 1 nm thickness increment. Thus, the calculated stress at a given depth approximates the local biaxial stress $\sigma_{zz}(z)$ defined in Eq. 2. Note that this calculation neglects any contribution of temporal relaxations to the force transients, instead assuming temporarily that the transients are entirely due to residual stress removal. Figs. 9 and 10 show the calculated residual stress distributions for the 20 V and 40 V anodic films, respectively. Both sets of profiles have steep apparent stress gradients within 1.5 nm of the oxide-solution interface, with relatively smaller stress at greater depths. The 1.5 nm surface layers correspond to the rapid stress relaxations in the first minute of dissolution in Figs. 5 and 6. At depths greater than 1.5 nm, the stress profiles measured in 0.4 and 1 M H₃PO₄ are in close agreement. The average stress at such depths in Fig. 9 is $-210$ MPa in the 0.4 M H₃PO₄ profile and $-190$ MPa in the 1 M H₃PO₄ profile. For the 40 V oxide in...
Fig. 10, the average stress is much smaller, −97 MPa in 0.4 M H₃PO₄ and −68 MPa in 1 M H₂PO₄. The measurement of similar stress levels in each solution, for both 20 V and 40 V oxides, provides quantitative evidence that residual stress removal controls the open-circuit force transients at times greater than 1 min.

The apparently elevated stress close to the oxide surface in Figs. 9 and 10 may be associated with temporal stress relaxations rather than removal of residual oxide stress. As mentioned earlier, this view is supported by the close agreement of force transients measured in 0.4 M and 1 M phosphoric acid, during the first minute of the open-circuit period (Figs. 4 and 5). In addition, it may be difficult to rationalize the large stress gradients near the oxide surface implied by literal interpretation of Figs. 9 and 10. If such gradients were present during anodizing, they would significantly perturb the oxygen ion migration rate. For example, the chemical potential gradient implied by the apparent near-surface stress gradient in the 0.4 M H₂PO₄ profile at 40 V, 1.8 GPa/nm, is equivalent to an electric field perturbation of 0.1 V/nm.6,40

During barrier oxide growth in 0.4 M H₂PO₄, the current density obeys an exponential high-field dependence on the electric field, \( i = i_0 \exp\left(\frac{BE_f}{k}\right) \), where \( E_f \) is the electric field in the oxide, and the value of the field coefficient is \( B = 23.4 \text{ nm}/V \).22 Accordingly, the fractional current density perturbation induced by the stress gradient would be \( \Delta i / i = B\Delta E_f / E_f \), or 230%. This large current density variation would violate charge continuity if not accompanied by a compensating space charge layer. However, we know of no independent evidence for such space charge layers. Therefore, the large near-surface stress gradients may be partly due to temporal stress relaxations during the first 1 min after current interruption.

Comparison of the 20 V and 40 V stress profiles and force transients reveal changes in stress relaxation mechanisms during barrier oxide growth. The residual stress profiles (depths greater than 1.5 nm in Figs. 9 and 10) measured in 0.4 M H₂PO₄ are considered most reliable for these purposes, as the 1 M H₂PO₄ force measurements were affected by fluctuations possibly caused by the higher dissolution rate. The residual compressive stress in the oxide is uniform at 20 V, while at 40 V the residual stress is reduced significantly and seems to be concentrated in the outer 20 nm of the oxide film. At 20 V, the force per width relaxes in the compressive direction by −0.7 N/m during the first minute on open circuit, and at 40 V the force per width relaxation is in the tensile direction by 1.4 N/m. Therefore, the increase of overall open circuit force change from 20 to 40 V (Figs. 5 and 6) corresponds to a larger transient force relaxation at the higher voltage; in contrast, the residual force in the thicker oxide phase-shifting interferometry. The open circuit stress change was significant larger than the electrostatic stress, and occurred over much longer time scales. The anodizing and open circuit stress changes were not affected by possible artifacts arising from thermal stress, internal stress in the metal samples, or stress induced by the dissolution reaction. At typical anodizing current densities (i.e., higher than 3 mA/cm²), oxide growth itself resulted in a compressive stress increase, while anodizing followed by complete oxide dissolution produced a net tensile stress change. The latter is due to tensile stress at the metal-oxide interface produced by metal oxidation. Tensile stress generation at open circuit following anodizing has been noted in earlier work, but attributed incorrectly to electrostatic stress or to open-circuit reactions involving the oxide. The net compressive stress usually measured during anodizing thus results from the summation of relatively large compressive and tensile contributions, from the oxide and metal respectively. The open-circuit stress measurements revealed contributions from residual stress in the oxide layer, as well as temporal stress relaxations on time scales of about 1 min. Stress monitoring during open-circuit dissolution was validated as an approach to measure residual stress distributions in anodic oxide films.

Conclusions

The present article reports in situ stress measurements during growth and open-circuit dissolution of anodic oxide films on aluminum in 0.4 M H₃PO₄ solution. Surface stress of Al sheet samples due to anodizing was deduced from curvature changes measured using phase-shifting interferometry. The open circuit stress change was significantly larger than the electrostatic stress, and occurred over much longer time scales. The anodizing and open circuit stress changes were not affected by possible artifacts arising from thermal stress, internal stress in the metal samples, or stress induced by the dissolution reaction. At typical anodizing current densities (i.e., higher than 3 mA/cm²), oxide growth itself resulted in a compressive stress increase, while anodizing followed by complete oxide dissolution produced a net tensile stress change. The latter is due to tensile stress at the metal-oxide interface produced by metal oxidation. Tensile stress generation at open circuit following anodizing has been noted in earlier work, but attributed incorrectly to electrostatic stress or to open-circuit reactions involving the oxide. The net compressive stress usually measured during anodizing thus results from the summation of relatively large compressive and tensile contributions, from the oxide and metal respectively. The open-circuit stress measurements revealed contributions from residual stress in the oxide layer, as well as temporal stress relaxations on time scales of about 1 min. Stress monitoring during open-circuit dissolution was validated as an approach to measure residual stress distributions in anodic oxide films.

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Implications of the stress measurements.—The open-circuit measurements in this work revealed that the net compressive force change during anodizing included a large tensile component remaining when the anodic film is dissolved completely, to leave an approximately 3 nm thick remaining oxide. The tensile force is attributed to stress near the metal-oxide interface, either in the metal or remaining oxide layer. However, if this stress were entirely localized in the oxide, the force changes in Fig. 3 would imply a stress as large as 5 GPa, which seems inconsistent with the much smaller compressive residual stress in the anodic oxide (Fig. 9). Therefore, we consider it more likely that the final force change is due to interfacial tensile stress in the Al metal generated by anodizing. Tensile metal stress near the interface could arise from formation of vacancies by anodizing, followed by elimination of the vacancies by climb of near-surface dislocations. Such a process was proposed by Suo and coworkers to help explain void formation during high-temperature oxidation.58 Several reports also suggest metal vacancy production during Al anodizing, such as near-interface metal diffusion during dilute Al-Au alloy oxidation.5,41 and observations of void formation close to the interface by positron annihilation measurements, transmission electron microscopy and atomic force microscopy.42,43 A quantitative treatment of interfacial metal diffusion accompanying anodizing will be reported in a separate article.

Tensile stress changes on open circuit following anodizing have been reported previously, but not in conjunction with characterization of open-circuit oxide dissolution. Hence, the tensile shift was attributed to processes within the anodic oxide. Vermilyea and Wüthrich suggested that the tensile stress change is due to dehydration of the outer hydrated portion of the oxide,23 and Bradhurst and Leach ascribed it to removal of electrostatic stress.44 These explanations cannot be valid in view our findings that the tensile open circuit force increases with anodizing current density (Fig. 3), and yet reaches its highest level when the oxide is almost completely dissolved (Figs. 1, 5 and 6). Previous papers have also significantly underestimated the compressive stress produced in the oxide by anodizing, since they did not consider the contribution of tensile interface stress to the measured force change.

The analysis of force changes during open-circuit dissolution also revealed temporal relaxations of the anodizing-induced stress. As the forming voltage increased from 20 to 40 V, the relaxations increased in magnitude, and changed direction from compressive to tensile. Relaxations of growth stress are frequently observed in thin-film deposition and electrodeposition experiments, and analysis of these relaxations has helped elucidate stress-generating mechanisms.17,24-26 In the present context of anodizing, both compressive relaxations of the tensile metal stress and tensile relaxations of the compressive oxide stress seem possible. The metal stress relaxation could be due to diffusion of Al atoms from interfacial voids to dislocations,42,43 while the oxide stress relaxation may be associated with diffusion of oxygen interstitial-like defects in the amorphous oxide to the external surface. Relaxation of metal and oxide stress would seem to predominate at low and high voltages, respectively. The stress relaxations will be discussed in greater detail in a subsequent paper.