Stress Distributions in Anodic Alumina Films Prior to the Onset of Pore Formation

Ö. Ö. Çapraz[1], Pranav Shrotriya[2], Kurt R. Hebert[1]

[1]*Department of Chemical & Biological Engineering,*
[2]*Department of Mechanical Engineering*
Iowa State University, Ames, IA 50011 USA

Porous anodic oxide (PAO) films are grown by electrochemical oxidation of valve metals in baths that dissolve the oxide. The self-organized hexagonal patterns of pores in these films have led to many investigations of PAO-based devices. However, the mechanisms of pore formation and ordering have not yet been fully explained. Recent experimental and modeling results indicate the importance of plastic flow during growth of self-ordered PAO.[1] Here we investigated the origin of stress driving plastic flow, and the possible role of stress in the morphological instability leading to pore formation. We report the first measurements of the evolution of stress distributions in barrier anodic oxide layers on Al, just prior to the appearance of pores.

In situ stress measurements were carried out with the curvature interferometry method, using 1 mm thick high-purity hard Al plates as samples. The Stoney equation was used to relate measured sample curvature changes to the force per unit sample width (biaxial in-plane stress integrated through the sample thickness). Anodizing was carried out at constant applied current density in 0.4 M H_3PO_4 solution at ambient temperature. Stress was measured continuously during anodic film growth and subsequent complete dissolution of the oxide at open circuit. Dissolution rates were determined by re-anodizing.

Fig. 1 shows force evolution during complete dissolution of oxides grown to potentials up to 40 V, at which the instability is first apparent.[2] The plotted force is relative to samples before anodizing. The negative value of each curve at zero dissolution time is the stress change during anodizing, and the final value represents a tensile stress increase in the metal. The anodizing stress change was in excellent agreement with prior measurements.[3] In some experiments, the anodic films were dissolved at different rates by increasing the acid concentration upon completion of anodizing. These results supported the interpretation of Fig. 1 in terms of residual stress profiles, where the local residual stress is the slope of the curve divided by the dissolution rate. The overall force change during dissolution represents the integrated stress in the oxide. Fig. 2 shows that both oxide and metal force changes increased with anodizing current density, indicating that both components of the stress are generated primarily by anodizing and not by open circuit dissolution.

At 10 V, Fig. 1 suggests that the oxide stress compressive and distributed across the film thickness. With further anodizing, the integrated compressive stress increases but the stress profile becomes increasingly localized near the oxide-solution interface, with nearly zero stress close to the metal. We conclude that the compressive stress is generated by reactions such as hydration at the solution interface, and not by Al oxidation. The concentrated compressive stress near the solution interface at 40 V is consistent with calculations of stress gradients needed to drive experimentally observed plastic flow.[1] We suggest that the tensile stress in the metal may be caused by Al metal vacancies produced by oxidation.
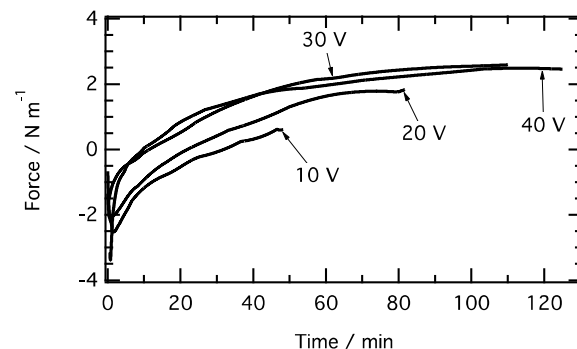

Figure 1. Stress change during open circuit dissolution for oxides formed at 5 mA cm^{-2} to various potentials (the ratio of oxide thickness to voltage is 1.1 nm/V).
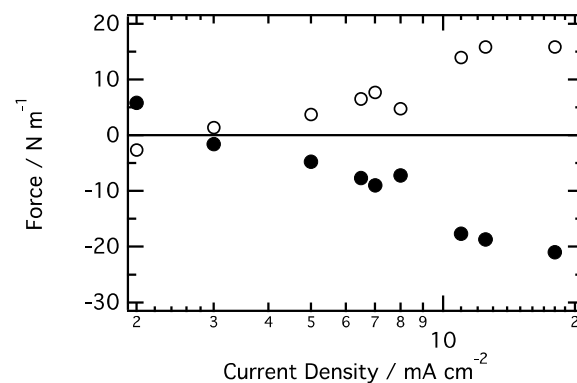

Figure 2: Metal (open circles) and oxide (filled circles) stress components after anodizing to 20 V at various current densities.

References
1. J. E. Houser and K. R. Hebert, *Nature Mater.* **8,** 415 (2009).
2. A. Baron-Wiechec et al., *J. Electrochem. Soc.,* **157,** C399 (2010).
3. Q. Van Overmeere, F. Blaffart and J. Proost, *Electrochem. Commun.,* **12,** 1174 (2010).