

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

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Porous anodic oxide (PAO) films are produced when reactive metals such as Al and Ti are electrochemically oxidized in baths that dissolve the oxide. Research in PAO-based devices has been stimulated by the self-organized hexagonally ordered pore arrays found for some anodizing conditions.¹ The initiation and ordering of pores follows a morphological instability of the initially planar barrier oxide, upon reaching a critical oxide thickness.²

In another presentation at this symposium, we present in situ stress measurements during galvanostatic growth of anodic barrier oxides on Al in 0.4 M H₃PO₄. Through-thickness profiles of the in-plane stress in the oxide were revealed for the first time, by monitoring stress change during open circuit dissolution following anodizing. It was shown that barrier oxide growth is accompanied by buildup of compressive in-plane stress. During this time, the stress profile becomes increasingly concentrated near the oxide-solution interface, such that a large gradient of ~ -1 GPa/nm is present at the time of pore initiation. The stress near the metal interface was nearly zero, revealing that stress is not due to the oxidation reaction, and the absence of stress change at current interruptions indicates that electrostriction stress is not significant. Instead, generation of compressive stress near the solution interface suggest that stress may be induced by hydration reactions.³ We observed that the compressive stress change in the oxide is accompanied by generation of tensile stress in the metal, at a ratio of -1.5 to -3.0 compressive/tensile.

Here we present a model for transport and stress generation in the barrier oxide that rationalizes these experimental observations. The model is based on concepts of point defects, as developed in studies of passive films.⁴ The major defects are oxygen and metal vacancies, produced respectively by Al oxidation and Al⁺³ dissolution. In addition we simulated hydration through the incorporation of oxygen interstitial defects at the film-solution interface. Oxygen interstitials and vacancies were mutually annihilated by reaction within the oxide.

The defect transport parameters were fit using both conduction and density measurements during Al anodizing.^{5,6} Calculations revealed that elevated vacancy concentrations approaching 15% of oxygen sites are produced at typical anodizing current densities of 1-10 mA/cm². The model proposed that these high vacancy

concentrations accelerate ionic transport by formation of pre-percolation vacancy clusters or micropores, that constitute "easy conduction paths." Indeed, such channels are revealed experimentally by oxygen isotope studies.⁷ The annihilation reaction between vacancies and interstitials impedes mass transport by removing easy conduction paths, and results in progressively concentrated compressive stress near the solution interface, as observed experimentally. The generation of compressive stress in the metal is quantitatively explained by the formation of metal atom vacancies by Al oxidation, and subsequent elimination of these vacancies by interaction with near-surface dislocations.

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