

Tailoring the Nanostructure Anodically Formed in the Passive Oxide on Aluminum – Relevance to Localized Corrosion Initiation

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Anodic processes at a passive metal surface like aluminum could be envisioned as being initiated or controlled by nano-scale structural changes within the metal's surface oxide. Examples include proposed roles for nanostructure formation in the pit initiation for Al corrosion (1,2), void formation on pit initiation of Al during anodic etching (3), and possibly deformation-induced nanostructure in pore formation in Al (4). Characterizing the nanostructure present in the passive oxide and learning how to control structure formation offers an opportunity to electrochemically explore deterministic relationships between known structure and anodic event initiation.

Recent work has shown that voids can nucleate at the aluminum/aluminum oxide interface and grow into the passive oxide at standard slow rate polarization in moderate chloride solutions well below the onset for pit initiation (5). Analytical transmission electron microscopy argues that these voids are encapsulated absence of matter produced by cation and anion vacancy saturation and coalescence in the oxide. Atomic force microscopy coupled with scanning electron microscopy show that these voids can transition to pores at efficiencies up to 20% of the void population or $2 \times 10^{10} \text{ cm}^{-2}$ prior to the initiation of pitting. These results demonstrate that interfacial voids are formed as a result of ion transport through the passive oxide and provide a foundation for exploring their role in pit initiation.

Most of this work has focused on anhydrous oxides to model the initial passive oxide on Al. These oxides are formed on atomically clean (vacuum prepared) bulk Al surfaces (both single and poly-crystalline) and nanocrystalline evaporated Al films exposed to O_2 at room temperature and atmospheric pressure. The length of time for equilibration of the model oxide in a de-aerated electrolyte is the factor that controls the extent to which voids and pores form. Time-of-flight secondary ion mass spectrometric (TOF-SIMS) measurements show that solution equilibration produces a slow growth of the initial 3 nm oxide up to an equilibration value of 4.5 nm over a period of 16 hours. Anodic polarization of the initial oxide produces a near-equivalent final thickness over a much faster time scale. It is this more rapidly formed film that exhibits a larger passive charge density (and larger void and pore densities) that exceeds values expected for uniform growth to its measured limiting thickness. The excess charge density has to be consumed either by vacancy generation (and subsequent coalescence) or dissolution. Dissolution alone appears an unlikely explanation given reported rates in a mixed chloride/borate electrolyte (6).

An initial attempt can be made to identify whether these structures play a role in pit initiation by exploiting this equilibration time effect. In limited cases, we have been able to show that higher density void nucleation produced by using shorter equilibration times can lead to high densities of pores that maintain a minimum (< 20 nm) diameter. It is this high density of transitioning features that might be expected to increase the probability of pitting event when compared the absence of detectable pores for long equilibration times. We have observed as

much as a 200 mV shift in the stable mean pitting potential to more active values with decreased equilibration time. Where these results provide an indication that voids and pores can contribute to pitting, they do not identify the necessity for these structures in a generalized pitting mechanism.

More recent work is focused on exploiting how the passive oxide is formed in an effort to tailor its resulting ion transmission characteristics and range of nanostructure exhibited. Our eventual goal is to learn how to control this nanostructure to a level where statistical studies of current transient events (i.e. metastable pitting events) can be correlated to characteristics of the feature population. Hydrated oxides produced by exposure of atomically clean Al to pure water vapor with and without subsequent dehydration show even larger variation in passive charge density response with anodic polarization. These results indicate that the initial characteristics of the oxide prior to immersion in the electrolyte could provide a wider range of control of structure density and size. The use of alternate electrolytes containing borate produces unique differences in the nanostructure population. One quite interesting effect of the borate anion is that TOF-SIMS and x-ray photoelectron spectroscopy show it attenuates the equilibrium concentration of chloride within the outer layer and/or at the barrier oxide interface in the passive oxide. Electrochemical impedance measurements indicate a reduced defect concentration within the barrier layer when borate is present while electron microscopy shows the void population is suppressed when borate anion is present. These results suggest that electrolyte composition can be used to control the nanostructure population as well.

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