

Interfacial Voids as Possible Precursor Sites for Pore Formation and Pitting in Aluminum

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The study of localized processes like pore and pit formation in Al is complicated by the apparent fact that the initiation and propagation stages are separated by potentially multiple concerted mechanisms of passive oxide property changes, dissolution, and local chemical and field enhancement, as examples. Fundamental knowledge about these stages is important in the quest to better understand the corrosion stability of Al as well as to utilize Al in nanotechnological applications. An attempt to relate the initiation and propagation stages could follow one of two possible paths: 1) pre-initiation events or features could be tracked up to the last detectable point and a relationship drawn to the early propagation stage or 2) propagation could be studied at progressively earlier time periods with relationships drawn toward the late initiation stage. This paper addresses the first possibility by attempting to identify and track nanostructure that forms in the passive oxide on Al under typical electrochemical conditions used to study pitting susceptibility.

The nanostructural features of interest are voids demonstrated to nucleate at the aluminum-oxide interface and grow into the passive oxide (1,2). The growth of the voids is related to the passive charge density generated upon slow scan rate ($0.17 \text{ mV}\cdot\text{s}^{-1}$) polarization in 50 mM de-aerated NaCl (pH 7) indicating that voids form as a result of material transport through the oxide. Of note is the fact that Cl^- is not necessary for void formation. We propose that the voids are a result of cation vacancy saturation at the metal-oxide interface resulting in a net relaxation energy to restore normal cation – anion spacing and the creation of internal surface area at the interface. These voids represent potential precursors for the formation of pores and pits due to their intrinsic occluded geometry. Whether stable pore or pit propagation actually initiates should be determined, in part, by the loss of the remnant passive oxide over the growing void.

The possibility that void growth could be linked to stable pore and pit propagation is demonstrated by correlating the electrochemical response of the passive oxide with its resulting nanoscale morphology. Figure 1 shows the polarization response of numerous sites on an Al(111) surface probed with a capillary electrochemical cell. This crystal was mechanically polished to $0.05 \mu\text{m}$ silica, subjected to ultrahigh vacuum annealing at 550°C for 2 hours, sequentially sputtered with low energy Ar and annealed (550°C) to remove the native oxide, and finally, exposed to $10^{13} \text{ torr}\cdot\text{sec}$ of O_2 in the vacuum processing environment. The data shown are for two sets of sites where the oxide was allowed to equilibrate at open circuit for either 60 or 600 minutes. The traces show that higher passive current density, an inflection in the current density, and a more cathodic pitting potential are exhibited by sites allowed only a short equilibration time. Longer equilibration produces much lower current densities, a much less significant current increase with applied potential, and a more anodic pitting potential.

These two classes of sites exhibit radically different nanoscale surface morphologies. Void populations were characterized using field emission secondary electron microscopy while the fraction of voids that had transitioned to pores was measured using contact mode

atomic force microscopy. The short term sites possess void densities up to $2 \times 10^{11} \text{ cm}^{-2}$ with maximum void diameters reaching 30 nm. The long term sites show much lower void densities of $2 \times 10^{10} \text{ cm}^{-2}$ and maximum void diameters of 7 nm. The AFM measurements for these short term sites yield pore densities in the range of 2 to $4 \times 10^{10} \text{ cm}^{-2}$ or a void-to-pore transition efficiency of 10 to 20%. The pore densities and/or diameters for the long term sites are apparently below the sampling criteria for our AFM approach. These larger pore densities for the short term sites suggest that the transition of the original void to a pore followed by pore growth correlate with the increased stable pitting susceptibility observed in Figure 1. The apparent absence of pores for equilibrated films could be rationalized in terms of the need for only one growing pore to give rise to stable pitting.

The fact that both the pore transition and continued growth are essential for initiating a stable, propagating event is demonstrated by the lack of a measurable discontinuity in pore density below and above the stable pitting threshold for a wide range of pure Al sample types. For example, a comparably prepared Al(110) sample exhibited pore densities as large as $2 \times 10^{10} \text{ cm}^{-2}$ for select sites irrespective of whether polarization was stopped below or at the stable pitting threshold. In addition, sites were also found where pitting had occurred and measured pore densities were less than $4 \times 10^9 \text{ cm}^{-2}$. These results suggest that the transition of a void is not solely sufficient for stable pit initiation for Al and that additional processes like pore growth are required for stable propagation of an event. Our current work is focused on describing void growth and transition kinetics in Cl^- , BO_3^{3-} and mixed $\text{Cl}^-/\text{BO}_3^{3-}$ solutions to better define this relationship between voids and early stage pit propagation.

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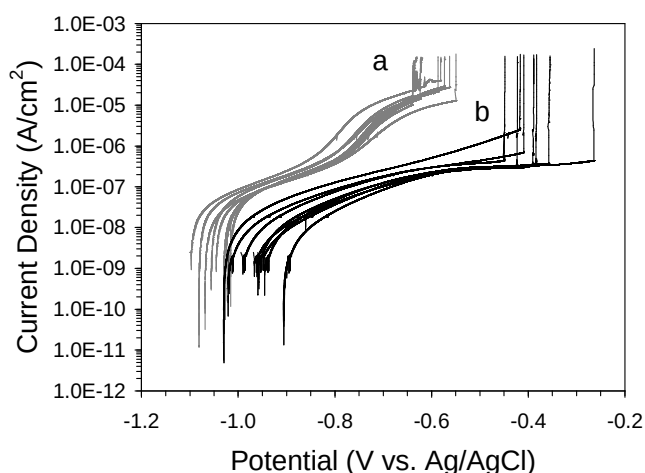


Figure 1. Polarization response for sites on an Al(111) surface in de-aerated 50 mM NaCl (pH 7) scanned at a rate of $0.17 \text{ mV}\cdot\text{s}^{-1}$: (a) after 60 min and (b) 600 min open circuit equilibration.