

Imaging and Characterizing Oxide Breakdown and Pit Initiation in Aluminum using Electron Microscopy

K.R. Zavadil

Sandia National Laboratories

P.O. Box 5800, Albuquerque NM, 87185-0888

Localized corrosion in passive metals, specifically pitting in aluminum, is a stochastic process. The factors responsible for pit initiation can be described but the nature and location of the pit precursor site, the site at which oxide breakdown occurs and a pit evolves, have eluded direct observation. The question is where does one look to observe a randomly occurring nanoscopic event? One approach to this problem is to design an experiment in which the imaging and electrochemical “fields of view” overlap spatially and are sufficiently small to provide the required resolution to drive, locate, and characterize the event site. We have chosen electron microscopy as a technique because of the high spatial resolution and the wealth of structural information it provides. We describe two separate experiments in this paper that represent a progression toward in situ electron microscopic visualization of early stage pit initiation in aluminum thin films. The composition of the initial oxide and the interfacial structure present at the amorphous passive oxide-aluminum interface are shown to be key attributes of determining where a pit is likely to nucleate.

Microelectrochemical methods are combined with electron microscopy using two separate approaches. The first type of experiment employs a microcapillary to define the electrochemical field of view. Chronopotentiometry conducted in a 10 micron diameter capillary on an Al(111) textured thin film in 50 mM NaCl(aq) produces just several pit nucleation events within a hundred to a thousand second time period, as shown in Figure 1. These events occur at potentials above the mean pitting potential observed for a macroscopic electrode area while the current required to polarize the microelectrode is only several picoampere. Given the low metastable pit nucleation frequencies reported for Al and low current, only few pitting events are actually expected to occur, consistent with observations (Fig. 1). Additionally, the magnitude of current available to substantially propagate the pit rapidly exceeds the value supplied in the experiment. These conditions produce a situation where capture of an early stage pit is more probable (1). The small size of the microcapillary defines the imaging field of view and we demonstrate that it is possible to locate early stage pits using scanning electron microscopy, as shown in Figure 2. Pits detected using this approach retain their original passive oxide layer as a membrane that covers the top of the pit. These membranes exhibit clusters of pores arrayed along the location of an original grain boundary. We define a pit precursor site as one in which this membrane has just started to form as evidenced by the appearance of pore clusters. Figure 2 shows an example of one of these precursor sites with its characteristic proximity to a grain boundary and clusters of pores. Extensive secondary and select cross-sectional transmission electron microscopic imaging shows that pore clusters are far more likely to form on the emergent facets from a grain boundary. We hypothesize that oxide-aluminum interfacial structural defects, such as steps, are responsible for lowering the energy required to nucleate the voids that lead to pore formation (1). Step density is expected to be greatest at these high angle facets in the (111) textured Al films.

These structural changes in the passive oxide can be studied in real time using TEM to image immersed Al microelectrodes. We demonstrate that it is possible to conduct on-column chronopotentiometric measurements using Al microelectrodes, comprised of (111) oriented grains, patterned onto electron transparent, amorphous silicon nitride membranes and integrated into a sealed microfluidic cell. Masking techniques are used to restrict the electrochemical field of view to equivalent diameters as used in our capillary measurements. Comparisons will be made between the early stage structural changes induced using these microcapillary and on-column approaches. Reports exist of the role of oxygen deficient-stoichiometry at the oxide-aluminum interface giving rise to a passive oxide more susceptible to chloride-induced breakdown (2). Decoupling the roles of interfacial structure (steps) versus oxide properties (interfacial oxygen vacancies) can be achieved by replacing the passive oxide created during processing under ambient conditions with oxides of known or pre-characterized interfacial composition. We contrast the response of ambient oxides with that of atomically clean aluminum surfaces exposed to molecular O₂ and activated forms of oxygen (e.g., atomic O).

This work is supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

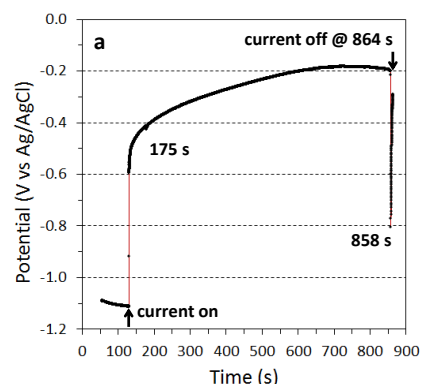


Figure 1. Chronopotentiometric curve produced by applying $4 \mu\text{A}\cdot\text{cm}^{-2}$ anodic current to an Al(111) thin film of 10 micron diameter area in 50 mM NaCl (pH 7.0). Two events occur at 175 and 858 s.

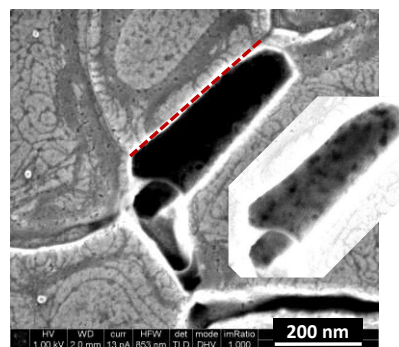


Figure 2. Secondary electron image of pit precursor site formed during the polarization shown in Fig. 1.

1. K.R. Zavadil, *Electrochem Soc Trans.* **41**, 133 (2012).
2. C.-L. Chang, et al. *J. Phys. Chem. C* **113**, 3502 (2009).