

## Localized Corrosion Initiation in Passive Thin Films

D.S. Elswick, J.J. Hren

North Carolina State University, Raleigh, NC

P.G. Kotula, D.F. Wall, N. Missert

Sandia National Laboratory, Albuquerque, NM

Pitting corrosion in Al occurs following breakdown of the passive oxide film. Several models explaining the initiation of localized attack have been proposed over the years, however, widespread agreement on pit initiation mechanisms is still lacking. This study uses high-resolution microanalysis to characterize the oxide layer in high purity aluminum, before and after pit initiation. Utilization of small area electrodes allows the observation of local changes occurring in the oxide before and after polarization to the pitting potential.

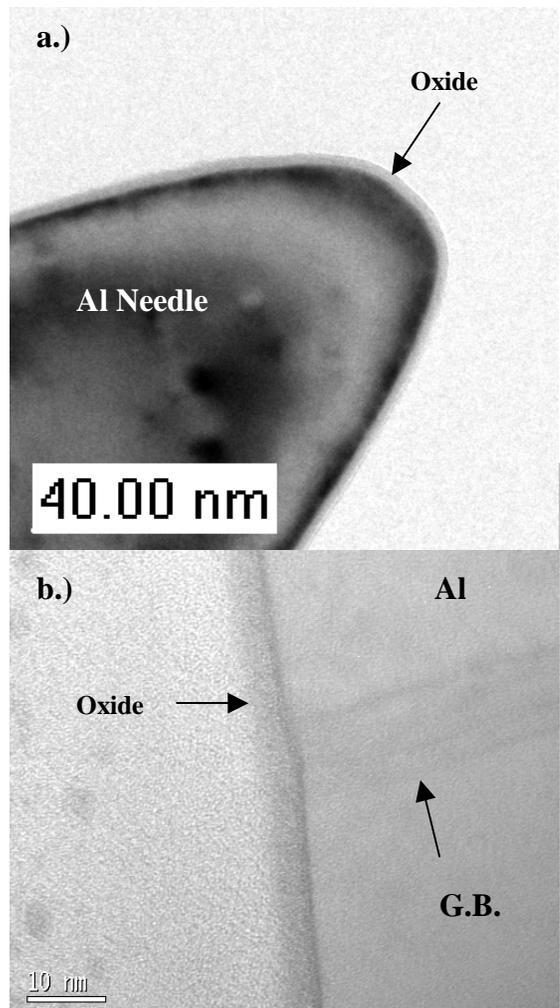
Two sample geometries were developed: high purity Al needles and multi-electrode wires embedded in epoxy. Both geometries minimize the area over which corrosion pits may initiate. Al needles localize the onset of corrosion pitting by defining a highly reactive area at which the attack occurs through an applied field. The multi-electrode samples are a cylindrical array of small, parallel Al wires, with a diameter of 125  $\mu\text{m}$ , embedded in epoxy. One end was prepared by cutting, mechanically polishing and electropolishing and the other ends of the wires provided electrical contacts. Electrochemical exposures were performed on both sample geometries, followed by detailed characterization and analyses of the oxide films, the oxide-Al interface, and the Al substrate.

The analytical techniques utilized transmission electron microscopy (TEM) for both structural characterization and chemical microanalysis. Energy-filtered imaging and x-ray spectral imaging characterized the structure of both the oxide and the Al substrate. For both sample geometries the initial oxide was found to be uniform with a thickness of 4-5 nm, as seen in Figure 1. Note that there is no significant change in oxide thickness over the range of surface orientations present in the needle (Figure 1a) nor across the grain boundary (Figure 1b) in the flat specimen.

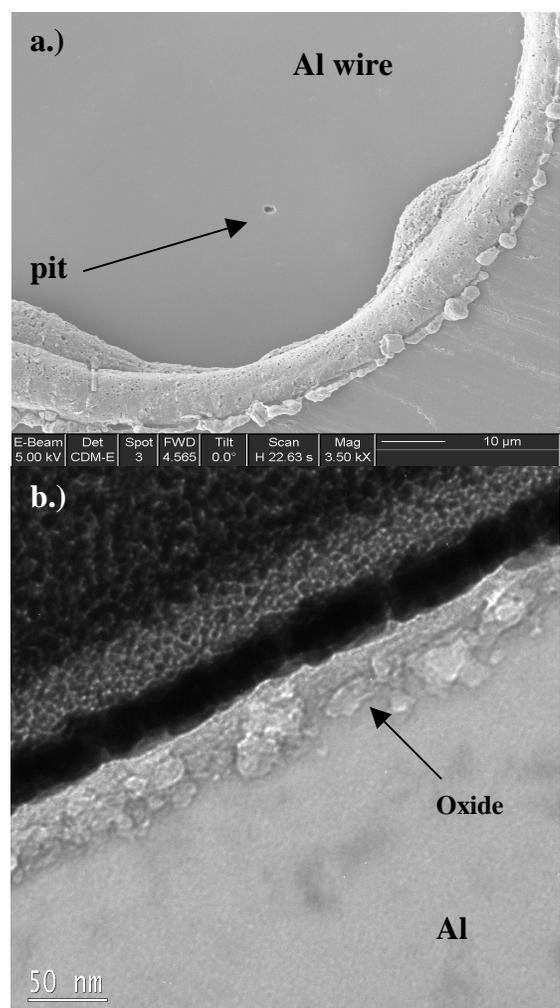
Samples were subjected to several conditions to initiate the corrosion process. Multi-electrode wires were addressed individually for pitting potential experiments and then examined using TEM. Figure 2 shows the results of one wire exposed to 0.05M  $\text{NaCl}_{\text{aq}}$  solution at room temperature with a constant potential scan of 0.1667 mV/s up to the pitting potential. A single pit formed as seen in Figure 2a. A TEM cross-section was made through the pit using dual-beam focused ion beam (FIB) technology. The TEM bright field image in Figure 2b shows that the oxide has apparently thickened by a factor of  $\sim 10$  and contains voids. Other results show a thickening and change in morphology of the oxide due to changes in both the chemical and electrical environments.

Jump ratio images of these same oxides did not convincingly demonstrate the presence of chlorine, but x-ray spectral image analysis [utilizing a fine probe to map out the spectra] indicated a Cl signal was present and that it was incorporated into the amorphous oxide/hydroxide structure. This suggests that chlorine plays a role in the corrosion process, but that the concentration levels have not yet been spatially localized. Attempts to obtain full electron energy loss spectroscopy (EELS) scans have not succeeded to date, due primarily to specimen damage at the 300 keV. Further experiments will be attempted at 100 keV where it is hoped that radiation effects can be greatly reduced.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Dept. of Energy under Contract DE-AC04-94AL85000.



**Figure 1.** Uniform initial oxide; 4-5 nm thickness **a.)** Needle geometry **b.)** Flat sample.



**Figure 2.** Multi-electrode sample exposed to pitting potential experiment. **a.)** SEM image of single pit formed. **b.)** TEM bright field image of surface area 1  $\mu\text{m}$  away from pit.