In Situ Study of Pit Initiation on Aluminum

Ainsley Pinkowitz
Graduate Student

Department of Materials Science and Engineering
Rensselaer Polytechnic Institute, Troy, NY, USA

Advisors: Dr. David Duquette and Dr. Robert Hull

Collaborators: S. Chee, S. Straub, B. Engler

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Background

- Aluminum is a passivating metal
  - Builds up a thin, tightly bound oxide film
- Passive films give good natural corrosion resistance
- The films are subject to attack
  - Total dissolution
  - Localized corrosion
Localized Corrosion

• Pitting, crevice, occluded geometry corrosion, or de-alloying.

• Growth mechanisms are well understood
  – Breakdown in oxide film leaves local area of more active potential
  – Increase in metal cations from anodic reaction
  – Cl⁻ ions flock to the region for charge neutrality
  – Presence of the Cl⁻ encourages hydrolysis to form a metal-hydroxide compound, and H⁺.
  – The now-acidic environment accelerates and stabilizes the process.

• Initiation mechanisms are not.
Initiation

- Best accepted theories:
  - Penetration
  - Adsorption
  - Film breaking

Observing the mechanism

• Until now, no tool existed capable of visualizing the initiation of a pit.
• Liquid cell holder allows a nano-scale corrosion experiment inside the TEM.
• Features a channel for flow and three electrodes for biasing.
Goals of in situ technique

• Al oxide film in solution is hydrated, and is modified by being dehydrated.
• TEM provides the resolution to observe pits at the instant of initiation.
• Much of the literature looks at stable pits, but metastable pits form and heal at lower potentials.
TEM resolution

Left: Al film under 250nm of fluid, at the corner of the viewing window.
Right: Al film dry

Al before (a) and after (b) 2 days exposure to vapor in the fluid cell (c) under 500nm fluid
Preliminary results

- Work is being done on the macroscale to establish conditions for pitting on the nanoscale
- Study on pitting potential as solutions become more dilute
Preliminary Results

• Work in TEM currently focused on expanding corrosion region, removing galvanic effects

Above: portions of the sample chip after linear potential sweeps. On left: chip with Ti deposited under the Al at the contact.
Future work

• Studies in the TEM will try to correlate pits to structural information
  – Grain boundaries, dislocations, stacking faults etc.
• EDS, EELS useful for correlating pits to local chemical makeup
• Varying conditions will be used to grow oxide films
  – Films’ reactions to being hydrated will be observed.
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