

## Surface Analysis of the Oxide Film on Aluminum Single Crystals Exposed to Chloride Solutions

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### INTRODUCTION

Localized corrosion, resulting from the exposure of metals with passive oxide films to environments with aggressive anions such as chloride, reduces the service life and reliability of these materials, leading to premature or catastrophic failures. The role that the aggressive anions play in the breakdown of passive oxide films on metals and alloys leading to localized corrosion is still a major unanswered question.

Passivating oxides inhibit the corrosion of technologically applicable metals such as aluminum, titanium, and stainless steel. Aggressive anionic species (e.g.,  $\text{Cl}^-$ ,  $\text{Br}^-$ ) are detrimental to passive behavior, resulting in accelerated corrosion, and often ultimately leading to the failure of the engineered structures. The onset of stable pitting on a passive metal such as aluminum (Al) usually occurs at a critical pitting potential,  $E_{\text{pit}}$ . However, potentiodynamic experiments on polycrystalline Al show a considerable scatter of  $E_{\text{pit}}$  values. The scatter of Al  $E_{\text{pit}}$  values may be attributed to variations in crystallographic orientations of the metal electrodes.

This goal of this research is to determine the role of the chloride ion interaction with the passive oxide film, and its effect on oxide film breakdown and pitting. Surface analytical techniques such as X-ray photoelectron spectroscopy and x-ray absorption spectroscopy will be used to follow chloride uptake by the passive film on aluminum single crystals at potentials below the pitting potential.

### EXPERIMENTAL PROCEDURE

High purity (99.999+ %) Al single crystals in the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  orientations were tested in a three-electrode electrochemical cell. The cell was filled with de-aerated 0.1 M NaCl solution at room temperature, and used a saturated calomel reference electrode. To determine the  $E_{\text{pit}}$  values, a sample of each orientation was polarized using a potentiostat in +5 mV intervals from +0.05 V vs.  $E_{\text{ocp}}$  to the onset of stable pitting. The samples were kept at each potential for 30 minutes. After the pitting potentials were determined, other samples of each orientation were polarized at selected potentials below  $E_{\text{pit}}$ . These samples were immersed in NaCl solution for 12 hours, after which they were polarized for 1 hour at the appropriate potential. The samples were removed from solution, rinsed with water, and dried using nitrogen. Surface analysis of the polarized samples was conducted using x-ray photoelectron spectroscopy (XPS) with Mg  $K_{\alpha}$  X-rays, as well as x-ray absorption spectroscopy (XAS).

### RESULTS AND DISCUSSIONS

Anodic polarization experiments demonstrated that the  $E_{\text{pit}}$  values for these samples are reflective of their crystallographic orientation. The three crystallographic orientations tested for this experiment exhibited different pitting potentials close to the  $E_{\text{pit}}$  value of polycrystalline Al. The  $E_{\text{pit}}$  ( $111$ ) was lower (less positive) than that of either  $E_{\text{pit}}$  ( $100$ ) or  $E_{\text{pit}}$  ( $110$ ), indicating that the  $\langle 111 \rangle$  orientation is the least resistant to pitting corrosion.

XPS data for samples polarized above the pitting potential indicated the presence of two pairs of chloride ( $\text{Cl}$ )  $2p_{3/2}$ - $2p_{1/2}$  doublets. The lower binding energy  $\text{Cl}$  species has been related to  $\text{Cl}$  on the oxide surface, while

the higher binding energy species has been associated with  $\text{Cl}$  incorporated in the oxide bulk.

XAS data supported the conclusion that there were two contributions from  $\text{Cl}^-$ , as the surface component was clearly distinguishable at 2832 eV from the bulk component at 2836 eV. (See Figure 1) Fluorescence XANES indicated that the maximum  $\text{Cl}$  concentration was reached 150 mV below the pitting potential, which is consistent with the results of the previous polycrystalline work.

This paper will discuss the x-ray photoelectron spectroscopy and x-ray absorption spectroscopy data for samples polarized at selected potentials below the pitting potential and the role of the chloride ion on passive film breakdown.

Figure 1. XANES spectra of the  $\text{Cl}^-$  K-edge on Al  $\langle 110 \rangle$  single crystal illustrating the features due to  $\text{Cl}^-$  at the oxide surface (at 2832 eV) and  $\text{Cl}^-$  in the oxide bulk (at 2836 eV).

