

Modeling the Chloride Ion Attack of Aluminum Oxide by Experimental and Theoretical XANES Analysis

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Introduction

Yu et. al. (1) have used XAS (X-ray absorption spectroscopy) and XPS (X-ray photoelectron spectroscopy) to study the chloride ion ingress into the aluminum oxide layer. They determined that the first step in pitting corrosion is the adsorption of the chloride ions (Cl^-) onto the oxide film surface of the aluminum followed by incorporation into the oxide film and this is in agreement with previous work(2). They went on to show that the Cl^- is incorporated into the film and appears to move to the oxide metal interface. In the present work, theoretical calculations were carried out using the FEFF 8 program to calculate the theoretical XANES edge structures (X-ray absorption near edge spectroscopy). This allows for a detailed examination of the interactions of Cl^- with the oxide film and underlying metal and broadens the understanding based on the previous work of Yu et. al. (1).

Experimental

Polycrystalline aluminum samples were exposed to a deaerated, room temperature 0.1 M NaCl solution that was prepared with reagent grade NaCl in 18 M Ω cm water. A three-electrode electrochemical cell was used with a saturated calomel electrode (SCE) for the reference electrode and a platinum mesh as the counter electrode. Individual samples were polarized at -950, -850, -800, -750 and -700 mV vs. SCE. The samples were then removed from the solution and examined by XAS (1, 3) at the Cl K-edge on beamline X19-A at the National Synchrotron Light Source at Brookhaven National Laboratory.

The model structures were calculated using CrystalMaker[®], a crystal and molecular structures program, to generate the atomic coordinates used in FEFF 8 (4), the *ab initio* multiple-scattering X-ray absorption near edge structure and X-ray absorption fine structure code. This program allows us to calculate the interactions of Cl^- on the surface as well as inside a model oxide film and on the metal surface itself and to generate theoretical Cl K-edge spectra to simulate chloride ions interacting with and penetrating into the aluminum oxide film.

Results and Discussion

Several aluminum oxyhydroxide structures including diaspore, boehmite and gibbsite were used as oxide models for calculations. Theoretical calculations of the Cl K-edge were made for Cl^- in various possible positions in the oxide lattice structure where adsorption and migration of the Cl^- might occur and were compared with the XANES data for Cl^- from the polarized samples. The results of the theoretical XANES calculations with boehmite and gibbsite showed very little in common with the experimental XANES data. Diaspore simulations displayed much closer much to the experimental data,

leading us to conclude that the oxide film on aluminum has structures that are most similar to diaspore. The crystal structure of diaspore is shown in Figure 1 to illustrate the types of possible Cl sites. Diaspore is constructed of layers of interconnected octahedrons with two different oxygen sites; OH^- sites have hydrogen bound to the oxygen and O^{2-} sites are oxygens in the -2 oxidation state without hydrogen attached and make up the bridging sites of the octahedrons. In order to simulate the Cl^- attack and breakdown of the passive oxide film, models were constructed replacing an oxygen ion from either an OH^- or an O^{2-} site with a Cl^- . Comparisons of the theoretical and experimental spectra suggest that the OH^- in a recessed surface site is the most likely point of the initial attack by Cl^- . The comparisons also show Cl^- attacking different sites as a function of the potential and finally, that chloride is present at the oxide/metal interface.

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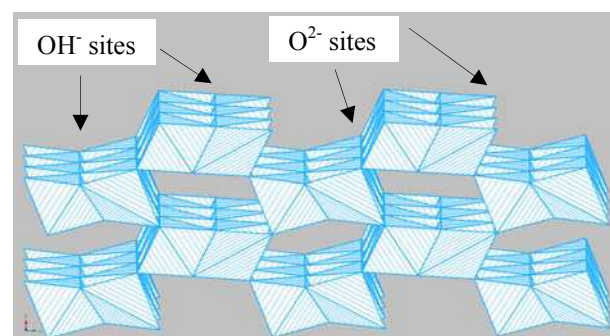


Figure 1. Diaspore is constructed of layers of octahedrons with two different oxygen sites.