Evolution of Oxide Stability During Localized Corrosion of Model Al-Cu Alloys

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Motivation—Al-Cu alloys are important for the aerospace, automobile, and micro-electronics industries. Although localized corrosion of aluminum-copper alloys in halide electrolytes is known to occur in the vicinity of intermetallic Cu-rich particles, a detailed understanding of the evolution of attack, from the mechanisms responsible for breakdown, to the transition to stable pitting, is still lacking. Since corrosion is a redox reaction, where the anodic oxidation of the metal must be balanced by the cathodic reduction of oxygen from solution, the mechanisms governing both processes must be understood in order to provide a complete picture. High cathodic reaction rates can generate local alkalinity, altering the properties of the passive oxide layer. Understanding the stability and charge transfer properties of the passive film in alkaline environments is therefore critical.

Accomplishment—We have used electron beam co-evaporated Al-3.5%Cu thin films as a model system for studying the effects of alkaline exposures on the loss of passivity in Al-Cu alloys. After annealing, Al_2Cu intermetallic particles form at grain boundaries in an Al-0.5%Cu matrix, with nanometer scale surface roughness as measured by AFM. In-situ fluorescence microscopy shows that initially, high cathodic reaction rates (which significantly raise the pH) occur locally on the electrode surface in response to remote anodic attack. The area available for high cathodic reaction rates continues to expand with time of exposure to the high pH solution, suggesting that exposure to the high pH environment enables more facile electron transfer to support high oxygen reduction reaction rates.

Areas exposed to the high pH environment (Figure 1) show localized attack adjacent to some particles, at grain boundaries and on grain faces, where an increase in attack site density is directly correlated to exposure time. Ex-situ AFM imaging shows no evidence for de-alloying of the particles or matrix even after a 30 minute exposure to pH 11.5, suggesting that on time scales important for corrosion initiation, an understanding of the evolution of oxide electronic conductivity as a function of pH is required. In order to evaluate the conductivity of the passive films, the current-voltage characteristics near the open circuit potential (OCP) were measured as a function of pH. The open circuit potential dropped as the pH increased, consistent with an increase in corrosion rate; that is an increase in both passive film oxidation rate and the balancing oxygen reduction rate. The slope of the cathodic branch, measured near the OCP, gives the polarization resistance, which decreased by over four orders of magnitude, as the pH increased from 6 to 11.5, demonstrating a huge activation of the surface for both the anodic and cathodic reactions. Electrochemical impedance spectroscopy (Figure 2) also showed a dramatic drop in the oxide impedance as the pH increased. The specific mechanism responsible for this activation is postulated to be a thinning of the surface oxide or an increased electronic conductivity, since Cu surface enrichment was ruled out through x-ray absorption, ToF-SIMS imaging, and cross-sectional TEM/EDS.

Significance—These studies show that the charge transfer properties of the passive oxide on Al-Cu alloys are sensitively dependent upon the solution pH. In alkaline environments, the charge transfer rates can increase by several orders of magnitude. These results will be used to develop accurate, predictive models for component lifetime and reliability limitations due to localized corrosion.

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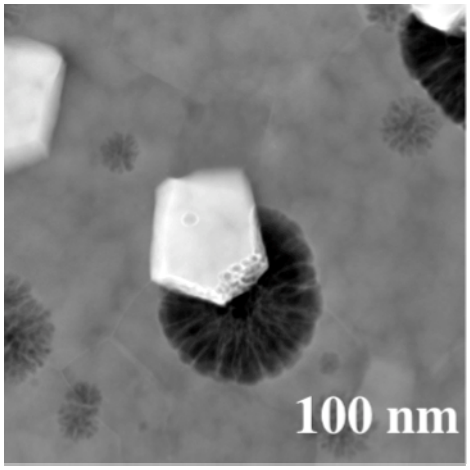

Figure 1. Early stages of localized attack on cathodic regions of the electrode occur on the grain faces, at grain boundaries, and at the interface between Al_2Cu intermetallic particles and the surrounding matrix.

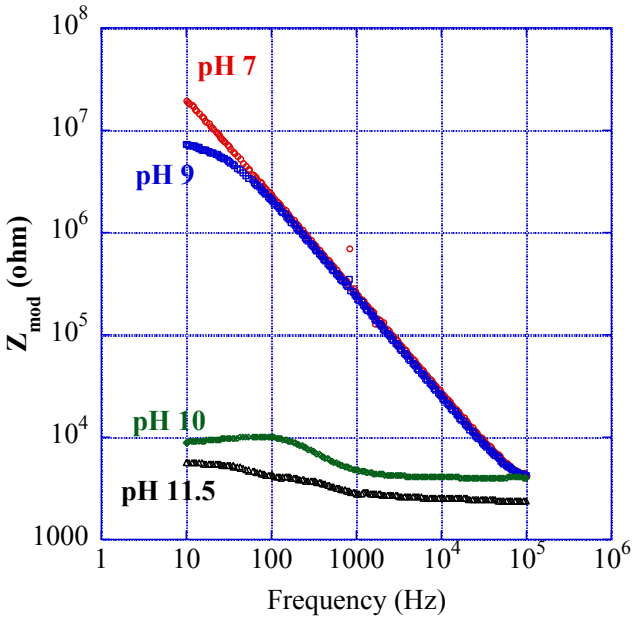

Figure 2. Electrochemical impedance spectroscopy showing several order of magnitude decrease in impedance with increasing alkalinity.