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# Electrochemical and Metal-Phase Processes Accompanying Hydrogen Absorption in Aluminum During Aqueous Corrosion

Kurt R. Hebert  
Iowa State University, krhebert@iastate.edu

Ömer Ö. Çapraz  
Iowa State University, capraz@iastate.edu

Pranav Shrotriya  
Iowa State University, shrotriy@iastate.edu

Guiping Zhang  
Iowa State University

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# Electrochemical and Metal-Phase Processes Accompanying Hydrogen Absorption in Aluminum During Aqueous Corrosion

## **Abstract**

Alkaline corrosion of aluminum results in large supersaturations of hydrogen, and formation of hydride and subsurface voids.<sup>1-4</sup> Aluminum itself is not susceptible to stress corrosion cracking (SCC), but hydrogen and hydride effects are significant for SCC mechanisms on Al and Mg alloys. Chu found evidence that corrosion-induced tensile stress in several alloys additively combines with external tensile stress to promote SCC, and attributed the former to lattice contraction associated with vacancies injected during corrosion.<sup>5</sup> Evidence for vacancy injection on Al was found from X-ray diffraction and in situ curvature measurements on Al thin films undergoing corrosion.<sup>1,6</sup> Here we report new measurements of stress evolution on Al sheet samples, over longer times than was possible with thin films. Also, we describe a model that provides a unified quantitative explanation of diverse experimental observations: electrochemical transients, stress measurements, hydrogen absorption detected by SIMS and void formation measured by positron annihilation spectroscopy (PAS).

## **Keywords**

Chemical and Biological Engineering

## **Disciplines**

Chemical Engineering | Electro-Mechanical Systems | Nanoscience and Nanotechnology

Electrochemical and Metal-Phase Processes  
Accompanying Hydrogen Absorption in Aluminum  
During Aqueous Corrosion

K. R. Hebert,<sup>a</sup> O. O. Çapraz,<sup>a</sup> P. Shrotriya,<sup>b</sup> G. P. Zhang<sup>a</sup>

<sup>a</sup>Department of Chemical and Biological Engineering

<sup>b</sup>Department of Mechanical Engineering

Iowa State University, Ames, IA 50011

Alkaline corrosion of aluminum results in large supersaturations of hydrogen, and formation of hydride and subsurface voids.<sup>1-4</sup> Aluminum itself is not susceptible to stress corrosion cracking (SCC), but hydrogen and hydride effects are significant for SCC mechanisms on Al and Mg alloys. Chu found evidence that corrosion-induced tensile stress in several alloys additively combines with external tensile stress to promote SCC, and attributed the former to lattice contraction associated with vacancies injected during corrosion.<sup>5</sup> Evidence for vacancy injection on Al was found from X-ray diffraction and in situ curvature measurements on Al thin films undergoing corrosion.<sup>1,6</sup> Here we report new measurements of stress evolution on Al sheet samples, over longer times than was possible with thin films. Also, we describe a model that provides a unified quantitative explanation of diverse experimental observations: electrochemical transients, stress measurements, hydrogen absorption detected by SIMS and void formation measured by positron annihilation spectroscopy (PAS).<sup>7</sup>

In situ stress evolution during open circuit alkaline dissolution was measured using curvature interferometry, on 1 mm thick hard 99.998% Al sheets. A reflective gold film was applied to the back side of the sample, which was in contact with air while the front side was exposed to solution. Curvature changes were measured through the interference between two laser beams, each of which reflected twice on the gold surface. Curvature was converted to stress-thickness product using the Stoney equation. Fig. 1 shows that cold-worked Al exhibited large rates of alkaline corrosion-induced tensile stress increase, similar to those of electron beam evaporated thin films.<sup>6</sup> Apparently this phenomenon is not restricted to certain types of samples. The initial rate of increase of the stress-thickness product was somewhat smaller than that of thin film samples, and did not depend significantly on pH or metal dissolution rate. However, comparable values of dissolution overpotential relative to the Al-oxide equilibrium were found at the two pH values, suggesting that the overpotential may control the rate of vacancy injection. A steady-state stress-thickness product was reached after 5-20 min that increased with pH. Experiments using annealed foils bonded to stiff substrates are being attempted to investigate the possible effect of vacancy-dislocation interactions on stress evolution.

The mathematical model of alkaline dissolution considered both electrochemical and metal-phase processes. Hydrogen and vacancy injection were modeled in terms of vacancy-hydrogen defects produced by corrosion.<sup>1</sup> These defects aggregated in the metal to form hydride particles that were subsequently exposed on the Al surface by selective metal dissolution. The model calculations successfully predicted open-circuit potential transients (Fig. 2) along with observations of time-dependent concentrations of metal vacancies detected by PAS and hydride particles found by SIMS and AFM.<sup>2,4</sup>

These results indicate chemical pathways to corrosion-induced tensile stress increases and hydride formation, factors that play important roles in SCC mechanisms.

#### ACKNOWLEDGMENT

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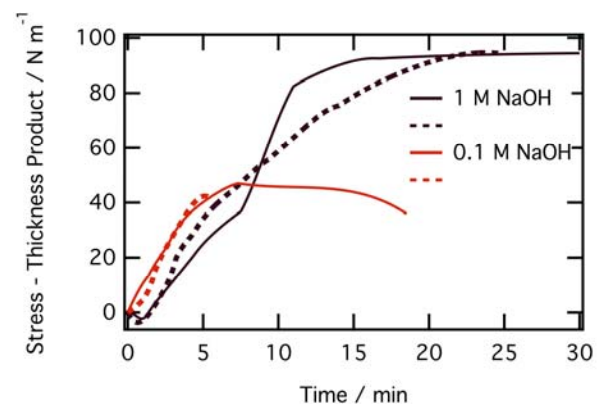


Figure 1. Stress evolution during Al dissolution in aqueous NaOH solutions at room temperature. Dashed curves demonstrate reproducibility.

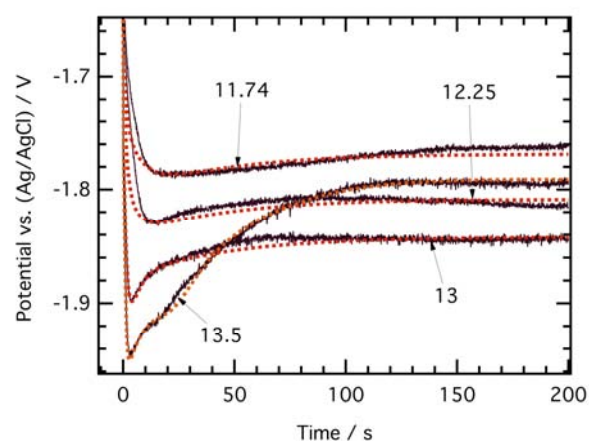


Figure 2. Experimental (solid lines) and calculated (dashed lines) potential transients during Al dissolution at the indicated pH values. Successive relaxation times in the transients are attributed to oxide dissolution (2 s), solution-phase diffusion (20 s), and the formation and dissolution of hydride particles (100 s).