Surface processes accompanying corrosion-induced hydrogen absorption into aluminum

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Abstract
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Keywords
alkaline dissolution, aluminum hydrides, hydrogen absorption, ion concentrations, surface processing, corrosion, high performance liquid chromatography, aluminum

Disciplines
Biochemical and Biomolecular Engineering | Biology and Biomimetic Materials

Comments

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Surface Processes Accompanying Corrosion-Induced Hydrogen Absorption into Aluminum

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The role of hydrogen-containing species in the alkaline dissolution of aluminum was studied by secondary ion mass spectrometry (SIMS). Large number densities of submicron particles nucleated and then disappeared during dissolution, at intervals of approximately 3 min. The particles were composed of aluminum hydride, with an aluminum hydroxide surface layer. When particles first appeared, the aluminate ion concentration near the surface was at the solubility of $\text{Al(OH)}_3$, and the potential was close to the Nernst potential for oxidation of $\text{AlH}_3$ to $\text{Al(OH)}_3$. The observed formation of $\text{AlH}_3$ indicates that the dissolving Al surface was poised near this equilibrium potential, i.e. that a hydride species serves as an intermediate in the dissolution process.

Introduction

Aluminum corrodes rapidly in alkaline solutions. Alkaline dissolution is technologically important as the Al electrode reaction in the aluminum-air battery, and is used to activate Al surfaces for anodic etching processes (1, 2). Since the dissolution potential is about 1 V cathodic to the hydrogen equilibrium potential, there is a large thermodynamic driving force for absorption of hydrogen. Large concentrations of about 1000 ppm of hydrogen have been measured in Al after alkaline dissolution (3, 4). Hydrogen absorption is accompanied by formation of near-surface voids which may contain hydrogen, and are relevant as pitting sites during anodic etching (5, 6). The chemical mechanism of hydrogen entry into metals, and the resulting formation of defects such as voids, are important for the fundamental understanding of hydrogen embrittlement. The present work focuses on the chemical role of hydrogen in the alkaline dissolution process.

Secondary ion mass spectrometry (SIMS) has been used extensively for characterization of surface and absorbed hydrogen in aluminum (7-10). This paper reports SIMS measurements of hydrogen-containing species on Al after dissolution. Unusual quasi-periodic "bursts" were observed in which high levels of hydrogen-containing secondary ions were present for brief periods. Atomic force microscopy (AFM) was used to correlate this transient behavior with the appearance and removal of nanoparticles on the Al surface. The results suggest the role of hydride surface species in the dissolution reaction.

Experimental
The Al samples were 110 µm thick foils of 99.99 % purity (Toyo). The foils were provided in the as-annealed condition with a typical grain size of 100 µm. In preparation for SIMS measurements, foils were first electropolished for 5 min in 20 % HClO₄ - ethanol solutions at 5 °C, at an applied potential of 30 V vs. a Pt counter electrode. Electropolishing was necessary to obtain a flat reference surface, to facilitate measurement of sputtered depth. Electropolished samples were further treated by open circuit dissolution for various times in 1 M NaOD (D₂O) at 25°C. Deuterated baths were used to eliminate interference from water vapor adsorbed from the atmosphere. ToF-SIMS was carried out at the Center for Microanalysis of Materials, University of Illinois at Urbana-Champaign, using a PHI Trift III instrument. The total transfer time between treatment and the initiation of sputtering ranged from 50 to 145 min. The samples were sputtered with a 15 kV Ga⁺ beam, and a 2 kV Cs⁺ beam was used to analyze negative secondary ions. The sputtered and analyzed areas were 400 x 400 µm and 50 x 50 µm, respectively. During depth profiling, the sample was sputtered for typically 5 s and then analyzed for 8 s. The sputtering rate in the metal was determined to be 0.23 nm/s, by measurement of the depth of a sputtered crater. The sputtering rate in the surface oxide layer was not measured.

Aluminum samples for atomic force microscopy (AFM) were prepared by immersion at open circuit in solutions of 1 M NaOH (H₂O) at room temperature. Imaging was carried out in direct contact mode, using a 14 µm scanner with Si cantilevers and a Si₃N₄ tip (Digital Instruments Nanoscope III). The photodiode voltage was set to 4.60 V; assuming a cantilever spring constant of 0.06 N/m, the estimated applied force was 1.5 nN. The scan area was 5 x 5 µm.

Results

Detection of Deuterium-Related Species with SIMS

Fig. 1 shows a set of depth profiles of negative secondary ions, from a 99.99 % Al sample after 14.5 min alkaline dissolution. The profiles of the major negative secondary ions from the oxide film (AlO -, O -) and metal (Al -, Al₂-) are shown, along with the deuterium-containing species (D-, AlD-, OD-). The peak masses of these species deviated by less than 0.002 amu from the respective theoretical masses. In Fig. 1, the depth of 5.8 nm corresponds to the decay of the AlO⁻ peak to half its maximum value, and also to a sharp decrease of slope of the Al₂⁻ signal. Based on prior work, these features identify this depth as the oxide-metal interface (7, 10). However, the true oxide thickness may not be 5.8 nm, since the depth calibration is based on the metal sputtering rate, which generally differs from that in the oxide.

Normalization of the counts of the D-containing species permits comparison of their profiles in samples treated for different times. For this purpose, signals were normalized with respect to the bulk metal level of Al₂⁻, which was the dominant peak in the metal in each sample. We made no attempt to determine sensitivity factors of these secondary ions, values of which are needed to compare profiles of different species in terms of concentration. The D⁻ profiles were nearly the same in as-electropolished samples and those treated in NaOD for any time. Since the electropolished samples had not been exposed to deuterium, the measured D⁻ profiles were evidently due to background contamination rather than alkaline dissolution.
Significant OD\(^-\) and AID\(^-\) peaks were not present in mass spectra of as-electropolished samples, but only after treatment in NaOD (D\(_2\)O). The OD\(^-\) and AID\(^-\) profiles also depended strongly on exposure time to the alkaline bath. Representative depth profiles of OD\(^-\) and AID\(^-\) in 99.99\% Al are shown in Figs. 2 and 3, for the as-electropolished foil and at dissolution times between 10 and 14.5 min. Both sets of profiles exhibited considerable but non-monotonic changes with dissolution time. For example, in Fig. 2, the AID\(^-\) profile was flat at 10 min, increased sharply at 12 min, decreased at 13 min and increased again at 14.5 min. When significant AID\(^-\) was present, the signal was low near the surface, rose to a maximum at 10-20 nm, and then decayed, approaching a constant value at roughly 60 nm. In contrast, the OD\(^-\) profiles were confined to depths less than 4 nm, and did not overlap significantly with the AID\(^-\) profiles.

A large number of dissolution experiments were carried out to characterize the dissolution time dependence of the AID\(^-\) and OD\(^-\) profiles. Figs. 4-5 show the thicknesses and integrated areas of the profiles after different immersion times in NaOD (D\(_2\)O). The profile thickness was taken to be the depth at which the mass signal decayed to 1/e, or 36.8\%, of its maximum value. Integrated areas were obtained by numerical integration up to a depths of 10 nm (OD\(^-\)) or 60 nm (AID\(^-\)), after first subtracting the constant background signal approached at large depths. The profile thickness and integrated area were both set to zero when the normalized mass counts did not exceed the background noise level of 0.001 at any depth. According to Fig. 4, significant AID\(^-\) profiles were found only during discrete ranges of dissolution time, during which the AID\(^-\) profiles resembled those at 10 and 12 min in Fig. 2. In particular, the AID\(^-\) profile areas and thicknesses rose and fell together, in a series of approximately regular "bursts" at 1, 4, 7-8, 11-12 and 15 min. The duration of each burst was about 2 min, and individual bursts were separated by periods of 1-2 min when the AID\(^-\) signal was indistinguishable from background. The integrated areas and depths of the OD\(^-\) profiles are shown in Fig. 5. Bursts of OD\(^-\) were found which coincided with those of AID\(^-\) at 1, 4 and 8 min. However, no further bursts were observed after 8 min, as OD\(^-\) profiles were found at all times except 14 min. The measurements after 15 min suggests accumulation of OD\(^-\) on the surface.

Surface Topography Evolution

If the rate of formation of Al(OH)\(_4\)^- ions by dissolution exceeds the mass transport rate away from the metal surface, the solution would supersaturate, possibly leading to precipitation of solid Al(OH)\(_3\). A rotating disk electrode study of the alkaline dissolution of Al found that the surface is covered by a precipitated Al(OH)\(_3\) film (11). The transient bursts of OD\(^-\) and AID\(^-\) detected by SIMS may be associated with precipitation from the alkaline solution. Therefore, evidence for precipitation during alkaline dissolution was sought through an AFM study of Al surfaces exposed to NaOH (H\(_2\)O) baths. Images were acquired after dissolution of electropolished Al foils for times up to 10 min. Fig. 6 presents examples of such images at times of 1, 2 and 3 min, along with a field emission scanning electron microscope (FE-SEM) image of a sample dissolved for 4 min. The typical ridge-scallop topography of the electropolished Al surface is apparent, along with approximately round objects having diameters less than 100 nm. These objects are the same as the much less numerous white particles shown clearly in the FE-
SEM image of a sample after 4 min dissolution. The AFM images indicate that the number and size of the particles varied with dissolution time. The particles initially formed between 20 s and 1 min. At 2 min, the particles decreased in number density but grew in size, while both the size and number density decreased significantly from 2 to 3 min. Thus, the particle number density was high during the same range of times as the bursts of AlD⁻ and OD⁻ at 1 min.

Particle size distributions were compiled from the AFM images, in order to quantitatively characterize nucleation, growth and removal of particles. Each distribution was obtained using two or three 5 x 5 µm images from separate experiments at a given dissolution time, and included between 178 and 671 particles. The distributions are plotted in Fig. 7, with the particle numbers in each size category normalized to the same area of 25 µm². The distributions indicate significant increases in particle number density in the intervals 0-1 min and 7-8 min, and suggest that another sudden increase may also occur between 2-3 min. Again, these times correspond approximately to the bursts of AlD⁻ detected by SIMS. In each case, the new particles were smaller than 50 nm in diameter. The distributions indicate that each particle nucleation event was followed immediately by growth and then by particle removal. The time elapsed between particle nucleation and removal was about 2 min, similar to the duration of the AlD⁻ bursts. Therefore, both the timing and duration of the precipitation events are consistent with the AlD⁻ and OD⁻ bursts detected by SIMS.

Fig. 8 shows heights and radii of individual particles, from the distributions at times from 5 to 8 min. At 5, 6 and 7 min, the particle heights are similarly distributed between 5 and 20 min. However, the range of particle heights at 8 min, is notably larger, 5 to 40 nm. The increase of the average height of particles between 7 and 8 min again corresponds to the rapid elevation of AlD⁻ and OD⁻ signals detected by SIMS.

Discussion

A simple mass transport calculation was carried out to determine whether the time at which particles first appeared is in fact consistent with Al(OD)₃ precipitation. Measurements of the rate of decrease of sample thickness indicated that the Al dissolution rate was approximately 2 nm/s. Hence the time of precipitation tₚ was estimated using Sand's equation,

$$t_P = \frac{\pi D (\frac{C_s \Omega_{Al}}{2v_d})^2}{2}$$

[1]

where $D$ is the diffusion coefficient of Al(OH)₄⁻ ions, $C_s$ is the concentration of Al(OH)₄⁻ ions at the metal surface when precipitation occurs, $\Omega_{Al}$ is the molar volume of aluminum (10 cm³/mol), and $v_d$ is the dissolution velocity (12). The diffusion coefficient of Al(OH)₄⁻ was reported by Heusler and Allgaier to be $8.4 \times 10^{-6}$ cm²/s (11). $C_s$ was taken as 0.05 M, the solubility of gibbsite, the least soluble form of Al(OH)₃ and normally the first precipitate from aqueous solution (13, 14). With these values, $t_P$ from Eq. 1 is found to be 40 s, in agreement with the time between 20 s and 1 min when the first precipitation
event occurred. Thus, the timing of the first appearance of particles is consistent with gibbsite precipitation at a small relative supersaturation.

The identities of chemical species associated with the OD\(^{-}\), AlD\(^{-}\) and D\(^{-}\) peaks are now considered. SIMS spectral peaks for OD\(^{-}\) secondary ions have been found to originate from passive films on Al containing deuteroxyl groups (7). While no reports of AlD\(^{-}\) or D\(^{-}\) peaks were found in the literature, secondary alane cations (AlH\(^{+}\), AlH\(_2\)\(^{+}\)) are formed by sputtering oxide-free Al surfaces exposed to hydrogen (15, 16). Under similar experimental conditions, aluminum hydride on the Al surface has been identified by infrared spectroscopy and scanning tunneling microscopy (17). Therefore, the AlD\(^{-}\) peak is not due to deuteroxyl groups in the surface film, and is more likely attributable to an aluminum hydride surface species. Evidence for the participation of hydride in Al dissolution was found earlier by Perrault (18). He showed that the pH dependence of the open circuit potential of Al could be quantitatively understood in terms of equilibria of reactions involving hydride species. In strongly alkaline solutions, the open-circuit potential was found to be determined by the equilibrium of

\[
\text{AlH}_3 + 3\text{OH}^- (aq) \rightarrow \text{Al} (\text{OH})_3 + 3\text{H}^+ (aq) + 6e^- \quad [2]
\]

The Nernst potential of this reaction, -1.95 V vs. Ag/AgCl at pH 14, is within 50 mV of the measured potential in the present experiments during the first 10 min of dissolution (Fig. 9). This indicates that the dissolution potential is consistent with the presence of deuteron on the Al surface. Additional indications of hydride on Al electrodes after polarization at cathodic potentials were found by Despic and co-workers (19, 20).

According to the AFM results, particles first appeared when the Al(OH)\(_4\)\(^{-}\) concentration adjacent to the Al surface exceeded the solubility of Al(OH)\(_3\). This result alone would suggest that the particles are precipitated Al(OH)\(_3\). However, the heights of particles (up to 40 nm) were much greater than the depths of OD\(^{-}\) profiles (about 3 nm), but comparable with those of the AlD\(^{-}\) profiles (30 - 40 nm). Therefore, the SIMS results indicate that the particles were not Al(OH)\(_3\), but instead were composed primarily of AlD\(_3\). The formation of AlD\(_3\) from supersaturated Al(OD)\(_4\)\(^{-}\) ions is thermodynamically possible, given the equilibrium of reaction 2 above. At the dissolution time of 1 min when particles are formed, the measured potential was -1.95 V, in excellent agreement with the Nernst potential of this reaction (Fig. 9).

While the times of AlD\(^{-}\) and OD\(^{-}\) bursts were correlated, OD\(^{-}\) was present only near the surface, while AlD\(^{-}\) was found at greater depths. Therefore, the OD\(^{-}\) measurements are consistent with Al(OD)\(_3\) films of several nanometers thickness, on the surface of AlD\(_3\) particles. These films were possibly formed by the reaction of the unstable deuteride with D\(_2\)O. This reaction would eventually decompose the particles, and probably accounts for their removal at the end of each burst.

Support for the proposed particle composition can be found in earlier field emission scanning Auger microprobe (FE-SAM) measurements (2). Particles formed by alkaline dissolution of 99.99% purity Al foils were examined, before and after sputtering to depths of 5 and 10 nm. Particle surface composition was compared to those of nearby sites where no particles were present. The spectra indicated that the particles were coated with a roughly 5 nm thick oxide or hydroxide layer. However, at the depth of 10 nm, the
same O/Al ratio of 0.3 was found on the particles as that on non-particle sites. On the latter sites, sputtering would have penetrated well below the 3 nm-thick surface oxide, and so the measured oxygen was due only to preferential sputtering of O relative to Al. Thus, according to the FE-SAM measurements, the particles were covered with oxide/hydroxide films, but their interiors were apparently metallic. However, since hydrogen cannot be detected by Auger spectroscopy, these results are also consistent with AlH₃ particles with surface oxide layers. Therefore, the Auger measurements support the proposed interpretation of the SIMS and AFM experiments.

The present experiments show that aluminum hydride nanoparticles are formed spontaneously during alkaline dissolution of aluminum, when the solubility of Al(OH)₃ is exceeded. The formation of hydride upon supersaturation with aluminate ions indicates that the surface is poised near an equilibrium condition between hydride and hydroxide/aluminate, as expressed by reaction 2. Therefore, our results suggest that aluminum dissolution occurs through a hydride surface species as an intermediate. The participation of hydride species in Al dissolution was proposed earlier by other researchers on the basis of electrochemical experiments (18-20). Our results, however, are the first surface analytical measurements supporting the presence of hydride during dissolution. Further, since OD⁻ would be found in a surface oxide or hydroxide film present during dissolution, its absence at times between the bursts suggests that the dissolving surface is not covered by such a film, up to 5-10 min dissolution times.

Conclusions

During corrosion of aluminum in 1 M NaOH(D), large number densities of submicron particles spontaneously appeared on the surface at quasi-periodic intervals of about 3 min. SIMS indicated that the particles are composed of AlH₃, and are covered with a hydroxide film. Particles are initially formed close to the time when the concentration of aluminate ions near the dissolving surface reaches the solubility of Al(OH)₃. From a thermodynamic point of view, the formation of hydride can be explained by the close proximity of the dissolution potential to the Nernst potential for the oxidation of hydride to hydroxide. Thus, the present results indicate that alkaline dissolution of Al occurs through a hydride surface species as an intermediate. The direct participation of hydrogen in the dissolution reaction provides a possible route by which hydrogen-vacancy defects can be continuously formed, and this in turn could explain the formation of subsurface voids (5).

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References


Figure 1. SIMS profiles after caustic dissolution of 99.99% Al for 14.5 min.

Figure 2. Representative AlD⁻ depth profiles after alkaline dissolution of 99.99% Al. Normalization is with respect to bulk Al₂⁻ counts.
Figure 3. Representative OD$^-$ depth profiles after alkaline dissolution of 99.99% Al. Normalization is with respect to bulk Al$_2^-$ counts.

Figure 4. Integrated AlD$^-$ depth profiles and profile thicknesses. Open symbols are averages of two data points at the same time.
Figure 5. Integrated OD depth profiles and profile thicknesses. Open symbols are averages of two data points at the same time.

Figure 6. Microscopic images of Al surface topography after alkaline dissolution. (a-c) 5 x 5 μm AFM top view images after 1, 2 and 3 min dissolution, respectively. Conversion of color scale to height is indicated below each image. (d) 2.5 x 1.7 μm FE-SEM image after 4 min dissolution (sample was dipped in 1 M HNO₃ solution after alkaline treatment).
Figure 7. Particle size distributions at various dissolution times, obtained by analysis of AFM images. Particle radius is defined according to $\sqrt{(\text{Area})/\pi}$. Number of particles in each size category is referenced to an Al surface area of 25 $\mu$m$^2$. 

Figure 7 continues...
Figure 8. Heights and radii of individual particles, measured by AFM after dissolution times from 5 to 8 min.

Figure 9. Open circuit potential during dissolution in 1 M NaOH (H₂O).