Electron Microscopic Observations of Interfacial Voids in Aluminum Created by Alkaline Dissolution

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Abstract
We report evidence from electron microscopy and positron annihilation spectroscopy (PAS) for the formation by alkaline dissolution of nm-scale voids in aluminum near the metal-oxide interface. Imaging was carried out using transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and field emission scanning electron microscopy (FESEM). EM images supported the PAS finding that voids were found within tens of nm of the interface, and revealed that the void number density increased by at least 10 times due to dissolution. From TEM, void number densities were on the order of 108 cm-2. From TEM and SEM, voids appeared circular in cross-section and were ~ 20 nm in diameter.

Keywords
electron microscopy, positron annihilation spectroscopy (PAS), interfacial voids, aluminum, alkaline dissolution

Disciplines
Biochemical and Biomolecular Engineering | Biological Engineering | Biology and Biomimetic Materials | Materials Chemistry

Comments

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We report evidence from electron microscopy and positron annihilation spectroscopy (PAS) for the formation by alkaline dissolution of nm-scale voids in aluminum near the metal-oxide interface. Imaging was carried out using transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and field emission scanning electron microscopy (FE-SEM). EM images supported the PAS finding that voids were found within tens of nm of the interface, and revealed that the void number density increased by at least 10 times due to dissolution. From TEM, void number densities were on the order of $10^8$ cm$^{-2}$. From TEM and SEM, voids appeared circular in cross-section and were ~ 20 nm in diameter.

Introduction

Recent positron annihilation spectroscopy (PAS) investigations have given evidence of nm-scale voids present in aluminum metal, located between 50-100 nm from the oxide-metal interface (1-3). Such interfacial voids can be formed by alkaline or acid dissolution or anodic oxidation of aluminum. PAS results also indicated that the internal surface of these voids was oxide-free suggesting their easy susceptibility to corrosion when exposed, and potential relevance as initiation sites for localized corrosion. Comparison between void number densities and pit nucleation rates supported the ability of voids to serve as pit-initiation sites (4). Indirect microscopic evidence for interfacial voids was obtained using anodic oxide replicas of the void-containing surface layer (5). Buckley and Birnbaum co-workers found substantial hydrogen absorption accompanying the formation of voids in the interior of Al foils, due to extended periods of alkaline dissolution (6-8). They concluded that the hydrogen was injected during open circuit caustic dissolution as H-vacancy defects, which agglomerated to form hydrogen bubbles or voids. The similarity of their experimental conditions and those in References (1-5) suggests that the formation mechanism may be similar.

In the present work, direct imaging of interfacial voids formed in aluminum during alkaline dissolution was attempted, using TEM and STEM. Additional microscopic observations by FE-SEM are reported, following removal of controlled depths of metal to expose subsurface voids. The microscopy results are compared to PAS measurements on samples subject to the same surface preparation. The information
from PAS and microscopy are complementary, in that PAS reveals global characteristics of the void population, while microscopy yields details of the geometry and location of voids.

**Experimental**

The aluminum samples were 110 µm thick foils of 99.99% purity (Toyo). The foil (henceforth referred to as 4N foil) was provided in the as-annealed condition and the typical grain size was 100 µm. Prior to the alkaline dissolution, all foils were electropolished in a 20% perchloric acid (70%) and ethanol (98%) bath at 5 °C for 5 min. Electropolishing was done to remove voids present in the as-annealed state of these samples, and to facilitate electron microscopy observations. The alkaline treatment was carried out in aerated 1 M NaOH solution at open circuit, for various times at 21 °C. After the dissolution, the samples were removed and rinsed with deionized water to stop the reaction and then air-dried.

To prepare samples for transmission and scanning/transmission electron microscopy (TEM, STEM) observations, the NaOH-treated or as-electropolished samples were thinned from the back (unreacted) side using a single-jet electropolisher, until the sample was perforated. The treated side was not exposed to the polishing solution during the thinning process. The electron-transparent regions close to the hole were then imaged using Philips CM30 scanning transmission electron microscope and a FEI-Tecnai G2-F20 scanning transmission electron microscope. The thickness of these regions was roughly 100 nm.

The preparation procedure for FE-SEM samples was (i) electropolishing; (ii) NaOH dissolution; (iii) anodizing in 0.1 M boric acid and 0.05 M sodium borate solution (pH ~ 8.8), at a constant applied current of 1 mA/cm², until attaining voltages of 7, 31 and 69 against the counter electrode corresponding to depths of 5 nm, 23 nm, and 50 nm of metal reacted; (iv) stripping the oxide in a 5 % chromic- 20% phosphoric acid bath at 70 °C for 2 min. All solutions were made using reagent grade chemicals and nanopure water.

Doppler broadening PAS measurements were done using a slow positron beam system at the University of Missouri-Kansas City. The spectrum of gamma radiation was measured at 2000 cps with a germanium solid-state detector having an energy resolution of 1.5 keV at the annihilation photopeak energy of 511 keV. The positron source was 50 mCi ²²Na.

**Results and Discussion**

**Positron Annihilation Spectroscopy**

A typical PAS S-parameter vs. beam energy (~ implantation depth) is shown in Fig. 1 for electropolished Al foils treated for three representative NaOH treatment times. All S-values were normalized against the bulk S-value, representing a defect-free reference. The top scale represents the mean implantation depths of the positrons, which is controlled by the beam energy.
\[ z_m = 14.8E_b^{1.6} \]

Figure 1. PAS lineshape parameter S vs. beam energy for 99.99% electropolished Al foils after different times of sodium hydroxide dissolution.

S-values greater than one in the metal indicate annihilation events occurring at open volume defects like vacancies and nm-scale voids. Fig. 1 clearly indicates the presence of open volume defects in the metal up to depths of the order of 100 nm. The oxide layer is found to be about 2-5 nm thick, and in Fig. 1 it is represented by the region with characteristic S values of less than 1 (9). Similar defect containing regions were indicated by S-energy profiles for several sodium hydroxide treatment times between 0-30 min.

The W-parameter vs. S-parameter plot for the 4N electropolished foil is shown in Fig. 2 below. S and W values for all the experiments fall along two straight-line segments connecting 3 vertices. The leftmost point (lowest S values) represents annihilation within the oxide layer, and the rightmost points (highest S values) correspond to annihilation in the defect-containing layer. The points then move along the lower straight line from right to left with the vertices corresponding to the defect layer and the aluminum bulk. The S and W parameters for the defect layer (rightmost vertex) as seen from the plot are 1.045 and 0.95, respectively (10). The presence of straight lines in the S-W plot values indicated that there was only one defect type present in all the samples. The high S and low W values indicated that these defects were voids of at least 1 nm in size whose inner surfaces were free of oxide (1). PAS of as-annealed Al, as-annealed samples after NaOH treatment (1), anodic oxidation (2) or acid dissolution (3) also reveal subsurface metallic voids.
Quantitative analysis of the spatial distribution of defects was done by fitting the S profiles to a solution of the diffusion-annihilation equation for positrons in a solid, using the software application VEPFIT. The simulation assumed a uniform void-containing layer adjacent to the oxide-metal interface. It yielded fit values of the characteristic S-parameter ($S_d$) and thickness ($B_d$) of the defect layer. Fit values of defect layer parameters for various dissolution times in NaOH for the 4N electropolished foil are shown in Fig. 3 below. The value of $S_d$ is determined by the defect type and its volume fraction. Since Fig. 2 shows that voids are the only defect, the variations of $S_d$ in the figure reflect changes in the void volume fraction. Thus, the void volume fraction seems to have a maximum value around 2-4 min of NaOH dissolution time, and then decayed slowly. The defect layer thickness was around 60 nm in most cases, with some scatter.

All the PAS studies indicated the presence of a void layer in the metal beneath the oxide-metal interface within 50-100 nm from the interface. Indirect and direct imaging of these voids was then attempted to reveal the geometry and location of the voids. Since the maximum $S_d$ value was seen to be at about 3 min NaOH dissolution time, this sample was chosen for most microscopic investigations using FE-SEM, TEM or STEM.
Electron Microscopy

Electropolished aluminum foils treated in NaOH for 3 min were anodized in a borate buffer solution at constant current density. This would oxidize known depths of the void-containing defect layer. The overlying anodic oxide was then stripped in a chromic-phosphoric acid solution. Fig. 4 below shows FE-SEM images of a foil anodized up to depths of (a, b) 5 nm, (c) 23 nm, and (d) 50 nm respectively after the NaOH treatment. A large number of circular cavities, most of which around 20 nm, in size can be clearly seen in the images (a) and (b), for which the sample was oxidized up to a depth of 5 nm. The number density of these cavities is on the order of $10^9$ cm$^{-2}$. These cavities were not seen in samples that were treated in NaOH for the same duration of time but not oxidized. Fig. 4 also clearly shows that the number density of cavities decreases significantly when the oxidized metal depth is increased to 22.5 and 50 nm. This indicates that the objects producing the cavities are found in a metal layer of less than 20 nm thickness from the oxide-metal interface. This depth is similar to the estimated void-containing defect layer thickness obtained from the PAS simulation results. Thus, the cavities could be metal voids exposed at the metal surface by oxidation followed by oxide removal. From the micrographs, it appears that these objects are preferentially found near ridges created by the alkaline dissolution treatment, although a number of them are also located in the scalloped depressions between ridges.
Figure 4. FE-SEM images of 4N electropolished Al foil treated in NaOH for 3 min with
(a) 5 nm (45° stage tilt), (b) 5 nm (0° stage tilt), (c) 23 nm (0° stage tilt) and (d) 50 nm (0°
stage tilt) metal anodized and the anodic oxide stripped chemically. SEM accelerating
voltage was 15-25 keV.

TEM imaging of the same 3 min alkaline treated electropolished foils was then
done after thinning the sampled from the back (unreacted) side, protecting the defect
layer formed during the NaOH dissolution process. Fig. 5 below shows TEM
micrographs of the same region on a sample before and after tilting the sample slightly.
The sample reveals the presence of small circular features 10-20 nm in size. Tilting of the
sample about the Bragg diffraction condition revealed changes in contrast consistent with
what is expected for small voids (11), i.e. the objects changed from light to dark. Tilting
in this manner is equivalent to obtaining "through focus" images, the method commonly
used to identify voids. The response of the voids to tilt was substantially different from
the contrast exhibited by nearby dislocations, which could be made to become invisible
while the voids were always visible.
Figure 5. TEM images of 4N electropolished foils treated in NaOH for 3 min. The images are of the same region with one of them slightly tilted. Accelerating voltage was 200 keV.

Figure 6. STEM image of 4N electropolished foils treated in NaOH for 3 min. for the same region as shown in the TEM image of Fig.5

Fig. 6 shows a STEM image of the same general region imaged by TEM as shown in Fig. 5, for the 3 min NaOH treated sample. It again indicates the presence of similarly sized features at these locations. The greater field of view reveals a higher number of such features than the TEM images. The scalloped surface of the samples apparent in the SEM images is also seen clearly in the STEM image.
Since the PAS studies indicated an S-parameter of more than one even for the as-electropolished samples, some voids are also expected to be seen in TEM images for these samples. While a few features like those seen for the treated samples were discovered in the untreated sample, the number observed (as determined from about 20 micrographs), was at least ten times smaller than that in the treated samples (as determined from around 40 micrographs with a total imaged area of about 25 µm²). The order of magnitude of the void number density was estimated at $10^8$ cm⁻² for the treated sample. These values corroborate the PAS observation that the void number density, indicated by the defect layer S-parameter, increased significantly due to the NaOH treatment (Fig. 3). The void number density in the treated sample is about an order of magnitude lower than the value from SEM.

In order to rule out beam-induced void formation, the same 3 min treated sample was imaged in the TEM using lower beam currents of 150 keV as compared to 200 keV used for the images in Fig. 5. Again, as shown in Fig. 7 below, similar features 10-20 nm in size were observed for the treated sample, while they were far less numerous in the untreated sample at the same voltage.

![Figure 7. TEM images of 4N electropolished foil treated in NaOH for 3 min. Accelerating voltage was 150 keV.](image)

Conclusions

The PAS studies show that a void-containing defect layer is found beneath the oxide-metal interface for the electropolished aluminum foil. This layer is tens of nanometers thick. The FE-SEM, TEM and STEM images provide direct evidence of the presence of such voids, and show that the number density of voids increases by at least ten times as a result of alkaline treatment. The voids seen using all the electron microscopic techniques were circular in cross-section and around 20 nm in diameter. The
alkaline dissolution generates a surface topography consisting of ridges surrounding scalloped depressions. Voids were preferentially located near these ridges, an indication that their formation is coupled to the dissolution mechanism.

Acknowledgments

This work was supported by St. Jude Medical Corporation and by the National Science Foundation through grant DMR-0605957.

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