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Effect of Impurities on Interfacial Void Formation in Aluminum

Abstract

The effect of impurities on formation of interfacial metallic voids, during uniform dissolution of aluminum in 1 M NaOH, was investigated. These voids are thought to act as initiation sites for pitting. Foils of three different bulk purities were used: 99.98% (3N), 99.997% (4N), and 99.9995% (5N). Positron Annihilation Spectroscopy (PAS) and Atomic Force Microscopy (AFM) revealed that nm-scale voids were formed by dissolution in each foil. The void volume fraction increased to a maximum during dissolution, at a time which increased with foil purity. The concurrent accumulation of near-surface Cu and Fe impurities during caustic etching was characterized using Rutherford backscattering spectrometry (RBS). For the three foils, a correlation of void volume fraction with Cu surface concentration was suggested. Processes involving Cu impurities may then at least partly control the formation of voids.

Keywords

Interfacial voids, aluminum, pitting

Disciplines

Biochemical and Biomolecular Engineering | Biological and Chemical Physics | Chemical Engineering

Comments

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EFFECT OF IMPURITIES ON INTERFACIAL VOID FORMATION IN ALUMINUM

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The effect of impurities on formation of interfacial metallic voids, during uniform dissolution of aluminum in 1 M NaOH, was investigated. These voids are thought to act as initiation sites for pitting. Foils of three different bulk purities were used: 99.98% (3N), 99.997% (4N), and 99.9995% (5N). Positron Annihilation Spectroscopy (PAS) and Atomic Force Microscopy (AFM) revealed that nm-scale voids were formed by dissolution in each foil. The void volume fraction increased to a maximum during dissolution, at a time which increased with foil purity. The concurrent accumulation of near-surface Cu and Fe impurities during caustic etching was characterized using Rutherford backscattering spectrometry (RBS). For the three foils, a correlation of void volume fraction with Cu surface concentration was suggested. Processes involving Cu impurities may then at least partly control the formation of voids.

INTRODUCTION

Near-surface nanoscale voids were detected in 99.98% purity aluminum foils using positron annihilation spectroscopy (PAS) (1,2). The voids were located in the metal, within 10-100 nm of the metal-oxide film interface. The internal surface of the voids was shown to be free of oxide, suggesting it would be highly reactive upon exposure resulting from uniform corrosion processes. Voids were present in as-received annealed foils, and were also formed by dissolution processes such as caustic etching. Surface cavities were viewed using AFM after chemically stripping the oxide film; the depth and volume fraction of these cavities corresponded quantitatively with those of the buried voids revealed by PAS. The distribution of cavities on the surface was strongly comparable to that of corrosion pits formed in HCl solutions, suggesting that voids can function as pit sites.

Impurities such as copper and lead are found to have an important influence on the anodic etching of high purity aluminum foils for electrolytic capacitors (3,4). These impurities strongly promote pit formation during etching, and for this reason their bulk concentrations are carefully controlled, copper at 20-50 ppm and lead at 1-10 ppm. The evidence that the pit distribution is strongly influenced by impurities, and that voids can serve as pit sites, suggests the possibility that impurities can play a role in void formation. Previously, Wu and Hebert used RBS to analyze the surface composition of 99.98 % purity foils after a 1 M NaOH dissolution treatment (5). This treatment can be used to promote pitting, and also generates interfacial voids (1). The concentrations of iron, copper, and gallium accumulated at a constant rate during the treatment, within a layer a of nm-scale thickness adjacent to the metal-oxide interface. If no impurities were

lost by dissolution, the dependence of the surface impurity concentration on time would obey

$$C_{is} = C_{is}^0 + V_d C_{ib} t \quad [1]$$

where C_{is} is the surface concentration, C_{is}^0 the initial surface concentration, V_d the dissolution velocity and C_{ib} the bulk concentration. The values of C_{ib} determined from the C_{is} vs. t data were consistent with those expected from the overall foil purity. Ashitaka et al. investigated the behavior of impurities during electropolishing, etching, and anodizing surface treatments (3,4). They were found to generate enrichments of copper beneath the oxide film, similar to those inferred by Wu and Hebert.

The relationship between voids and impurities was examined in the present work. PAS, AFM and RBS were used concurrently to correlate impurity surface segregation and void formation. Since the impurity surface concentration is controlled by the product of dissolution time and the bulk concentration (Eq. 1), the effect of C_{is} on void formation was tested through the use of foils with three different bulk purities.

EXPERIMENTAL

The aluminum foils used in this work had overall bulk purities of 99.98% (3N), 99.997% (4N), and 99.9995% (5N), as reported by the manufacturer. All foils were approximately 100 μm thick. As-annealed 3N foils, with typical grain size of 100 μm, were provided by Nippon Chemi-Con (4). 4N and 5N foils (Alfa) were annealed at 550 °C for 6 hours and 10^{-7} Torr. Inductively Couple Plasma-Mass Spectrometry (ICP-MS) was used to measure the bulk concentrations of Cu and Fe impurities. Cu concentrations were found to be 7.4, 3.9, and 0.8 wt-ppm for 3N, 4N, and 5N foils, respectively, while Fe concentrations were 15.1, 4.4, and 14.2 wt-ppm in the same foils. Dissolution of aluminum foils in aqueous 1 M NaOH was carried out at room temperature and open circuit, without circulation of the bath. The dissolution velocities measured using a precision micrometer were 140, 130 and 73 nm/min for 3N, 4N and 5N foil respectively.

Positron Annihilation Spectroscopy (PAS) was used to detect near-surface voids in aluminum foils after NaOH dissolution. The measurements were conducted in a vacuum chamber at a pressure of about 10^{-7} Torr (1,2,6). A monoenergetic positron beam produced by a ^{22}Na source implanted positrons within the sample at a mean depth given by

$$z_m = 14.8 E_b^{1.6} \quad [2]$$

where z_m is in units of nanometers and the beam energy E_b is in keV. At each beam energy, a Doppler-broadened gamma radiation spectrum was measured using a Ge

detector mounted perpendicular to the beam direction. S and W spectral lineshape parameters were calculated by the system software. The VEPFIT software application was used to determine the effective defect layer S parameter, a measure of its void volume fraction (1,2). Surface composition was measured with Rutherford Backscattering Spectroscopy (Charles Evans). The RBS system used a He^{++} ion beam with energy 2.275 MeV, and the detector was oriented at an angle of 160°. AFM examination of foils was carried out in air and with contact mode (Digital Instruments Nanoscope III). Prior to AFM observation, some NaOH-treated foils were placed in solutions of chromic-phosphoric acid, in order to dissolve the surface oxide film. The chromic-phosphoric acid bath consisted of 2 wt % CrO_3 and 2 wt % H_3PO_4 at 85°C, and the immersion time was typically 1 min. Analysis of the areas of cavities formed by dissolution was carried out using the Image SXM software application.

RESULTS AND DISCUSSION

PAS Measurements

Fig. 1 shows the defect layer S parameter, S_d, vs. dissolution time for the 3N, 4N, and 5N foils. The fractional cavity mouth area vs. dissolution time (see next section) was

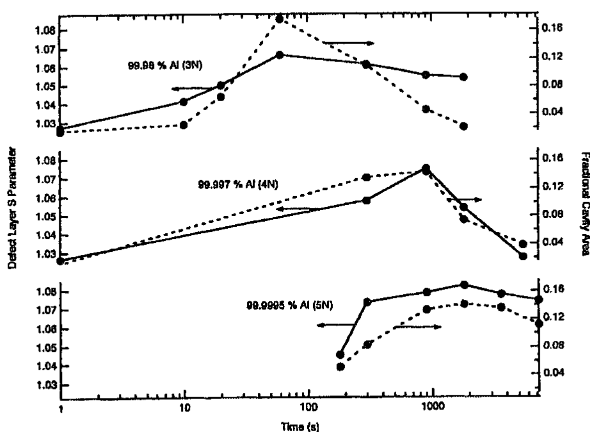

Figure 1. Change of PAS model defect layer S parameter and the fractional cavity mouth area with dissolution time for 3N, 4N and 5N foils.

also plotted in the figure. S_d reflects variations of the void volume in the defect layer. For each foil, S_d increases to a maximum value as dissolution proceeds, and thereafter declines slowly. The times of the S_d maxima were approximately 1, 15 and 30 min for 3N, 4N and 5N foils, respectively. Since the dissolution rates of the foils differed by only

about 30%, evidently the higher purity foils required a more dissolution to reach the maximum void volume fraction. This suggests a role for impurities in void formation, as discussed in more detail below.

AFM Topographic Images During Dissolution

Fig. 2 shows three pairs of AFM top-view images that depict surfaces of the three foils, before and after chemical stripping of the surface oxide in chromic-phosphoric acid.

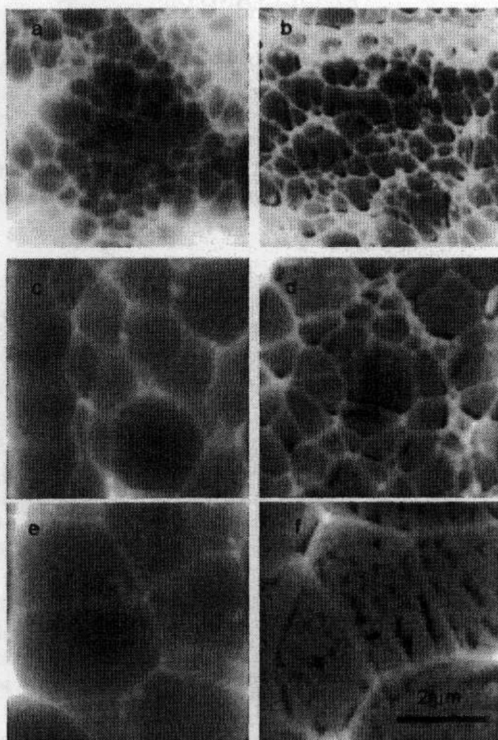

Figure 2. AFM images for foils before and after oxide stripping. (a) 3N foil, 900s in NaOH; (b) 3N foil, 900s in NaOH , followed by oxide stripping; (c) 4N foil, 1800s in NaOH; (d) 4N foil, 1800s in NaOH, followed by oxide stripping; (e) 5N foil, 7200s in NaOH; (f) 5N foil, 7200s in NaOH, followed by oxide stripping

The images demonstrate the "scalloped" topography formed by caustic dissolution, consisting of shallow depressions bordered by ridges. They indicate that oxide stripping in chromic-phosphoric acid did not change this topography, but instead revealed a number of cavities. The required stripping time for the appearance of cavities was about 1 min, significantly longer than that estimated from the film thickness of 3 nm and the oxide dissolution rate of 30 nm/min. Thus, while no extended corrosion was detected by weight loss measurements, a limited amount of metal dissolution may occurred during the exposure of cavities. Consistent with prior results on chemically polished aluminum, Fig. 2 demonstrates that the scallop width (distance between adjacent ridges) increased with bulk foil purity (7). This observation supports the suggestion that impurities are elevated on ridges compared to surface between ridges (7). It may be seen in Fig. 2 that cavities formed at locations near ridges on 3N and 4N foils, but that cavities in 5N foils showed no such preference.

The topography of AFM images, either with or without oxide stripping, showed similar trends with dissolution time. In the early stages of dissolution, large and isolated cavities were found, and the surface was generally roughened by dissolution. The scallop topography appeared on all three samples after minimum dissolution times of approximately 5 min for 3N and 4N foil and 15 min for 5N foil. The fractional surface area occupied by cavity mouths, determined using image analysis software, is plotted in Fig. 1 as a function of dissolution time. For each foil, the fractional cavity area and S_d have the same trend with dissolution time, with maxima occurring at the same times. This agreement is evidence that cavities form from buried voids, by uniform dissolution of the overlying oxide and possibly metal. It is apparent that cavities are not the product of a localized dissolution process in the oxide stripping solution.

Accumulation of Near-Surface Impurities during Dissolution

The surface impurity concentration after dissolution can be calculated by Eq. 1, which assumes retention of all impurities in the solid. In order to test this assumption for the case of Cu and Fe impurities, RBS was used to quantitatively characterize the surface composition of 3N and 4N foils, after respective dissolution times of 15 and 30 min. The spectra were compared to a simulation based on Eq. 1 with the additional assumption that the initial surface impurity concentration could be neglected (5). The simulation was implemented using the RUMP software package (Computer Graphic Service). The impurities were assumed to be distributed uniformly within a 10 nm thick, surface-adjacent layer. Within this layer, the impurity concentrations per unit area were determined by Eq. 1 with C_{is}^{0} set to zero. Ni was included in the simulation of the 5N foil, since it is present in the manufacturer's assay of impurities, and its energy edge lies between Cu and Fe. For a given set of area concentrations, the predicted spectra were insensitive to the layer thickness, for thickness smaller than 20 nm. Fig. 3 compares experimental and simulated spectra in the region of the Cu and Fe edges. Reasonable quantitative agreement is found, especially for the 4N foil. This agreement supports Eq. 1, and in particular, the assumption of Cu and Fe retention during dissolution.

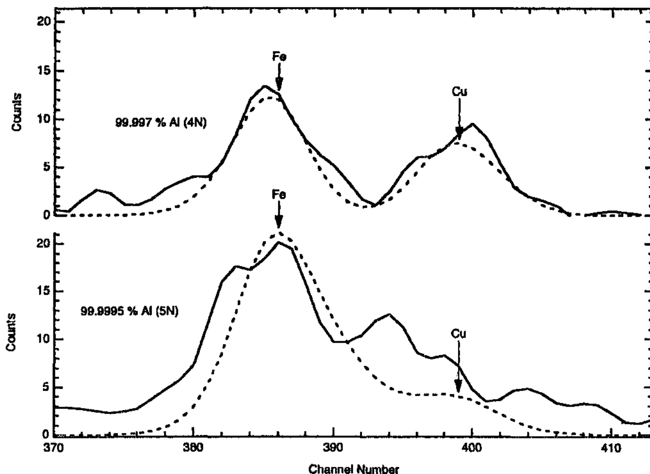

Figure 3. Portions of Rutherford backscattering spectrum for (a) 4N foil after 15 min dissolution in NaOH, (b) 5N foil after 30 min dissolution. Solid lines are experimental spectra and dashed lines simulated spectra

Near-Surface Voids and Impurities

The influence of surface impurities on void formation was explored by examining the correlation between Cu and Fe surface concentrations and the trends in Fig. 1. Fig. 4

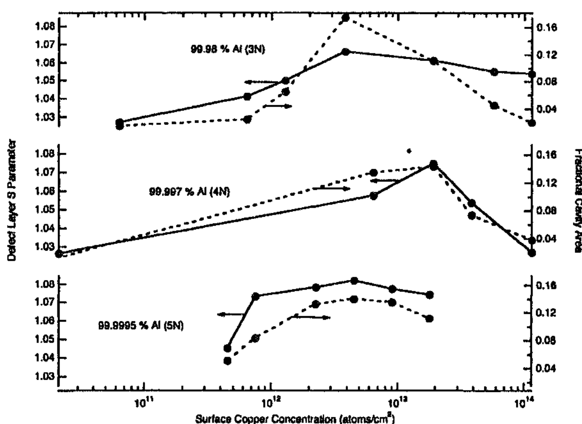

Figure 4. Defect layer S parameter and fractional cavity area vs. copper surface concentration from Eq. 1.

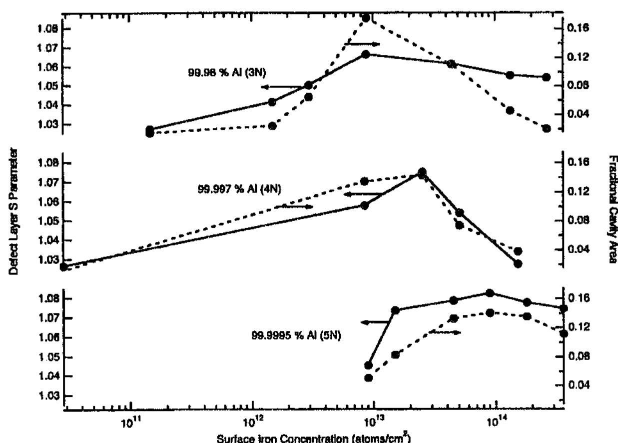

Figure 5. Defect layer S parameter and fractional cavity area vs. iron surface concentration from Eq. 1.

shows the defect layer S parameter and fractional void area plotted as a function of the surface Cu concentration from Eq. 1. The corresponding results for Fe are found in Fig. 5. Inspection of Figs. 4 and 5 indicates that the trends of S and cavity area for different purity foils are similar when plotted vs. copper concentration. There is a weaker correlation with Fe concentration. Thus, it is implied that the formation of voids is related not to dissolution time, but to the surface concentration of impurities such as Cu, which are accumulated near the surface by dissolution of aluminum. If voids serve as pit sites, this result could explain the importance of controlling the concentration of Cu impurities, in order to obtain a favorable distribution of etch pits. However, since the overall purity of the three foils but not specifically the copper concentration was controlled, it cannot be conclusively said whether voids are controlled by Cu, or some other impurity whose concentration scales with that of Cu.

Fehlosi et al. investigated the formation of voids by oxidation of various Al alloys, and proposed that interfacial void formation is controlled by the Pilling-Bedworth ratio (PBR) (8). PBR is the ratio of the volume of the impurity metal oxide produced at the metal-film interface, to the consumed metal volume. When PBR is less than 1, oxidation generates interfacial void volume; when it exceeds 1, oxidation produces excess interfacial oxide and thus compressive stress. It was concluded that the PBR for copper was likely greater than one, so that oxidation of interfacial copper metal would not form voids. In fact, the excess oxide formed by Cu oxidation might inhibit void formation by the oxidation of other impurities whose PBR is less than 1. In another paper, Caicedo-Martinez et al. reported that the oxidation of Cu atoms in Al-Cu alloys is controlled by the Cu surface concentration (9). Cu oxidation was found to initiate above a critical surface concentration of 2×10^{14} atoms/cm^2.

In Fig. 4, the critical concentration of 2×10^{14} atoms/cm^2 for copper oxidation appears on the extreme right of the graph, corresponding to very few voids and cavities. This is consistent with the idea that copper oxidation inhibits void formation. It is possible that the effect of copper oxidation is felt at smaller extents of dissolution, when the average surface concentration is below the critical value. As mentioned earlier, the scallop topography formed by dissolution first appears just before the maxima of S_d and fractional void area. Since the ridges between scallops are probably sites of locally elevated copper concentration (7), it is conceivable that the local Cu concentration on ridges reached 2×10^{14} atoms/cm^2, even before the average surface Cu concentration approached the critical value. Localized Cu oxidation on ridges might inhibit void formation there, and may thus control the decreasing void concentration after the maximum.

Fig. 4 suggests that surface Cu may also promote void formation, at small extents of dissolution prior to the initiation of Cu oxidation. Alloying impurities have been found to enhance void nucleation, and near-surface Cu atoms may function in this way (10). On the other hand, since in the present experiments the overall foil purity and not the Cu concentration is varied, the initial rise of void concentration may be due to an impurity other than Cu, whose concentration scales with the foil purity. For example, if this impurity has a PBR less than 1 and is either surface-segregated or has a low critical concentration for oxidation, its oxidation would produce interfacial voids at low extents of dissolution. Then, as dissolution proceeds, oxidation of Cu would eventually initiate, consuming the interfacial void volume generated by oxidation of the other impurity. This mechanism could explain the non-monotonic trend in Fig. 4.

CONCLUSIONS

The relationship was investigated between surface concentration of Cu and Fe impurities, and formation of interfacial metallic voids in aluminum. Previous work has pointed out evidence that such voids can act as pit initiation sites (5,6). Void formation and surface impurity accumulation during uniform dissolution of aluminum in 1 M NaOH were characterized, using RBS, AFM and PAS. Three types of aluminum foils with different bulk purity were used, which demonstrated different rates of surface impurity accumulation during dissolution. In each foil, PAS and AFM revealed evidence for generation of nm-scale interfacial voids at small dissolution times, and removal of such voids at long times. The accumulation of Cu and Fe near the Al surface during dissolution, without appreciable loss of these impurities to solution, was verified by RBS. are were formed by dissolution in each foil. It was found that the PAS and AFM measurements, when plotted vs. surface Cu concentration, showed a similar trend for all three foil purities. This suggests that processes involving Cu impurities at least partly control the formation and removal of voids as dissolution proceeds. This finding may explain the well-known effect of ppm-level Cu impurities on pit nucleation during aluminum etching.

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