Corrosion-Related Interfacial Defects Formed by Dissolution of Aluminum in Aqueous Phosphoric Acid

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Abstract
The mechanism was investigated by which pit initiation on aluminum foils during anodic etching is affected by the use of phosphoric acid as a pretreatment. Positron annihilation measurements, coupled with atomic force microscope images of foils with chemically stripped oxide layers, show evidence that the pretreatment introduces nanometer-scale voids in the metal, at or near the metal-oxide film interface. The location and morphology of voids compares favorably with those of pits, suggesting that voids act as pit initiation sites. The number of void sites was estimated to be $10^7 \text{cm}^{-2}$, the same magnitude as the maximum number of pits formed by anodic etching. Capacitance measurements further indicate that the treatment decreases the surface oxide thickness to about 2 nm. Formation of large numbers of pits during etching is promoted by either reduced oxide thicknesses or more positive etching potentials. It is suggested that the rate of initiation of pits at interfacial voids is determined by the electric field in the overlying surface oxide.

Keywords
aluminum, corrosion, voids (solid), anodisation, atomic force microscopy, positron annihilation, surface composition, surface structure, etching

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Comments

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Corrosion-Related Interfacial Defects Formed by Dissolution of Aluminum in Aqueous Phosphoric Acid

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The mechanism was investigated by which pit initiation on aluminum foils during anodic etching is affected by the use of phosphoric acid as a pretreatment. Positron annihilation measurements, coupled with atomic force microscope images of foils with chemically stripped oxide layers, show evidence that the pretreatment introduces nanometer-scale voids in the metal, at or near the metal-oxide film interface. The location and morphology of voids compares favorably with those of pits, suggesting that voids act as pit initiation sites. The number of void sites was estimated to be $10^7$ cm$^{-2}$, the same magnitude as the maximum number of pits formed at a portion of their internal surfaces were metallic and free of oxide. The measurements indicated that the voids were found either at the interface itself, or at depths below it up to about 100 nm; the term “interfacial voids” as used here encompasses either possible location.

Chemical dissolution of the oxide layer in chromic-phosphoric acid solution exposed 10-100 nm wide cavities, viewed with atomic force microscopy (AFM). “Cavity” in this context refers to these particular features revealed by oxide stripping and is used here to distinguish them from pits formed by anodic etching. Observable properties of the cavities such as their depth and area coverage were in agreement with positron measurements. The close relationship between cavities and voids is evidence that cavities form at voids during oxide stripping. A correspondence was also demonstrated between the cavity shapes and locations and those of pits formed during etching, suggesting that interfacial voids can serve as pit initiation sites. Presumably, dissolution of material covering the void would expose its reactive, oxide-free metallic surface, and rapid corrosion would then follow. Evidence from AFM has in fact been obtained that the appearance of a pit during anodic etching is preceded by dissolution of a few nanometers of metal around the pit site. Open-circuit dissolution of aluminum in 1 M NaOH, used as a pretreatment for the etching processes, was found to substantially increase the number of interfacial voids.

In the present study, the effect of phosphoric acid pretreatment on pit nucleation in aluminum was investigated. This treatment, like the caustic treatment, serves to increase the number of pits formed during subsequent anodic etching. The enhancement of pitting is demonstrated by scanning electron microscopy (SEM) of etched high-purity foils. The nature of pit precursor sites was studied by Doppler-broadening positron annihilation spectroscopy (PAS) and AFM, as was done in the earlier study of NaOH-treated foils. The present work thus explored whether the formation of interfacial voids occurs in other dissolution processes in addition to the caustic treatment. Also, the necessary conditions for the pretreatment to result in a significant increase in the pit number density were characterized in some detail. In particular, the effects of the treatment on both the number of interfacial voids and the oxide layer thickness were investigated and correlated with the enhancement of pitting. Results for both as-received and electropolished foils, which have different initial oxide thickness, are presented. The mechanism of pit initiation is discussed with regard to the role of interfacial voids and the effect of oxide thickness.

Experimental

The aluminum samples were nominally 99.98% purity annealed foils, 100 µm thick, with a typical grain size of 100 µm, manufactured for use in aluminum electrolytic capacitors (foils were provided by Nippon Chemi-Con). Composition measurements with spark-source mass spectrometry revealed bulk concentrations of Cr, Cu, Fe, Ga, Mg, Si, and Zn impurities on the order of 10 wt-ppm, confirming the order-of-magnitude impurity content indicated by the nominal purity. The large grain size found in such capacitor foils is due to extensive annealing treatments after rolling, e.g., for 5-6 h at 600°C. Normally, single grains span the foil thickness, as can be inferred from SEM observation of the morphology of etch tunnels, which grow along (100) directions. Tunnel shapes show no evidence of direction changes suggesting passage through grain boundaries.

Foils treated by phosphoric acid immersion were either in the as-received condition, or else were first electropolished. Electropolishing was normally carried out at a constant applied current density of 0.25 A/cm$^2$ in a phosphoric acid-ethanol-water bath at 40°C for times of 2.5-5 min. The foil dissolved completely in a time of...
tween 3–4 min, indicating that the dissolution rate was at least several micrometers per minute. In addition, one sample examined by PAS was electropolished in the Jacquet bath (22 vol% perchloric acid and 78 vol% acetic anhydride, 5-10°C) at 25 V for 3 min. For phosphoric acid treatment, foils were immersed in an 85°C, 5% H₃PO₄ bath at open circuit.

Anodic etching was at a constant applied potential of −0.35 V in 1 M HCl at 70°C and for a period of 0.1 s, unless otherwise specified. Just before etching and after H₃PO₄ treatment, the foils were dipped in 1 M H₂SO₄ at room temperature for 10 min, to stabilize their corrosion potentials. The etching cell utilized a platinum counter electrode and Ag/AgCl/4 N KCl reference electrode. All cited potentials are with respect to this reference, which is at 0.221 V vs. NHE. The etched surface morphology was observed using SEM (JEOL JSM-840A). Solutions for etching, as well as all electrochemical and chemical treatments, were prepared from reagent-grade chemicals and deionized water.

In order to ascertain changes in the oxide film thickness due to electropolishing and phosphoric acid treatment, the capacitance of treated foils was measured. Foils were transferred to a cell containing 0.1 M H₂SO₄ solution at room temperature, in which an anodic current density of 0.5 mA/cm² was applied. The potential transient during the early moments of anodic oxide growth was measured at time intervals of 0.01 or 0.02 ms using a high-speed voltmeter (Keithley 194A) interfaced to a computer. The capacitance was determined by dividing the applied current density by the average slope of the transient in the first 0.08 ms.

AFM examination of foils was carried out in air and with direct contact mode, using a 14 μm scanner along with Si cantilevers and a Si₃N₄ tip (Digital Instruments Nanoscope III). In some experiments, the oxide film was chemically stripped prior to AFM observation by immersing the foil in a 2 wt% Cr₂O₃-5 wt% H₃PO₄ bath at 85°C. During the course of the work, many duplicate images were acquired and the tip was replaced on a number of occasions. No effects of the tip condition on the image topography were revealed.

Positron measurements were conducted in a vacuum system at 10⁻⁷ Torr. The positrons are ejected from a ²²Na source and after moderation in W foil, emerged as a monoenergetic beam which implanted them within the sample to an energy-dependent mean depth. For annihilation in aluminum metal, the dependence of mean positron implantation depth z_m on beam energy E_b is given by

\[
z_m = 14.8E_b^{1.6}
\]

where depth is in nanometers and energy in kiloelectronvolts. At each beam energy, the spectrum of gamma radiation, due to annihilation of positrons by electrons, was measured using a Ge detector mounted perpendicular to the beam direction. S and W line shape parameters were calculated for the annihilation photon peak around 511 keV. This energy is the equivalent of the electron and positron masses, for the usual case of two photons formed by the annihilation. The broadening of the peak at around 511 keV is due to the Doppler shift of the photon energy associated with the momentum of the annihilating electron. For this reason, the peak shape is sensitive to the local distribution of electron momentum.

Each spectrum consisted of about 1 × 10⁶ photon counts, and 6 × 10⁵ counts in the photopeak. S and W were calculated by the system software to within an accuracy of 0.001. As consistent with conventional usage, the S parameter is proportional to the central area of the photopeak, which is contributed by annihilation of positrons with valence electrons. The W parameter is proportional to the area of the extremes of the photopeak and is due to annihilation by core electrons. Open-volume defects such as vacancies and voids are populated by valence electrons, and thus have relatively large S and small W parameters. During the time between the measurements of Ref. 3 and those in the present work, the gamma photon detector was modified, yielding an enhanced energy resolution. This improvement resulted in increased photon counts close to 511 keV, and the S parameter values were larger than those in Ref. 3 when identical samples were compared.

Results and Discussion

Positron annihilation measurements.—Doppler-broadening PAS was used to detect open-volume defects near the metal surface after H₃PO₄ treatment. Figures 1 and 2 show PAS measurements of the S parameter as a function of positron beam energy. The S-energy profiles in Fig. 1 are for as-received foils, while Fig. 2 shows foils electropolished in the phosphoric acid-ethanol-water bath. The mean implantation depth of positrons at each beam energy from Eq. 1 is shown on the top axis in each figure. S is normalized using the S parameter of the bulk aluminum, which should be a defect-free reference condition for these large-grain annealed foils. The absence of significant bulk defects is demonstrated by the bulk positron diffusion length of 150 nm needed to simulate these measurements, which is numerically consistent with the diffusion length of annealed single-crystal aluminum. The diffusion length decreases with concentration of vacancy-type defects, and the large value suggests a negligible defect concentration, as expected in equilibrium at ambient temperature. Normalized S values larger than one within the metal indicate the presence of open volume defects. S

![Figure 1](image1.png)

**Figure 1.** S parameter vs. energy profiles showing effect of phosphoric acid treatment time on unpolished foils.

![Figure 2](image2.png)

**Figure 2.** S parameter vs. energy profiles showing effect of phosphoric acid treatment time on electropolished foils.
layers. Positronium is an electron-positron bound state, and its heights of which increase strongly with $H_3PO_4$ implantation depths about the mean. The increase of the maximum of 10 keV and are associated with a layer of metal adjacent to the oxide with a thickness of the order of 100 nm, which contains open-volume defects. This thickness is smaller than the depth calculated from Eq. 1, since at 10 keV there is significant dispersion of implantation depths about the mean. The increase of the maximum $S$ value with phosphoric acid treatment time is due to changes in the nature of this defect layer. A similar increase of the $S$ peak was found during the first few minutes of NaOH treatment. The peak $S$ of the as-received foil, 1.036, is higher than the value of 1.028 reported in Ref. 3. As mentioned in the Experimental section, the $S$ parameters in this work are expected to be increased due to the improved detector energy resolution. Evidently, normalizing $S$ with respect to the bulk value did not fully resolve the differences resulting from the modified detector. That is, as a result of the improved resolution, the near-511 keV photon count increased proportionally more for spectra in the defect layer compared to those for bulk aluminum.

The profiles of the electropolished and phosphoric acid-treated foils in Fig. 2 also have near-surface regions with $S$ larger than one, but only when the $H_3PO_4$ treatment time is 15 s or longer. For treatment times less than 23 s, there are layers where $S$ is less than one, which extend to depths as great as 400 nm. Similar low-$S$ layers are found on aluminum with porous anodic oxides, and in fact thick surface oxides are expected after the phosphoric acid electropolish used here. The porosity of the oxide is revealed through examination of the $R$ parameter (Fig. 3), which represents radiation outside the 511 keV photopeak. The $R$ parameter is enhanced relative to bulk aluminum within the low-$S$ layers in Fig. 2. This elevated $R$ reveals significant formation of ortho-positronium (ortho-Ps) in the low-$S$ region, as was also the case for the porous alumina layers. Postironium is an electron-positron bound state, and ortho-Ps refers to its decay to three photons with energies away from the peak. Since ortho-Ps forms on surfaces, the enhanced $R$ is clear evidence of porosity in the oxide layer. The porous oxide on the electropolished foil is evidently removed by phosphoric acid treatments at least 23 s in duration. The thick oxide after the electropolish would have masked an $S$ peak arising from interface defects created during electropolishing. Hence, it is unclear to what extent the defects formed up to 23 s were introduced during either phosphoric acid treatment or electropolishing. After removal of the porous oxide at 23 s, the $S$ peak continues to grow significantly to 27 s, after which the maximum $S$ did not increase further up to 1 min.

To help identify the defect type in the foils shown in Fig. 1 and 2, a plot of $S$ vs. $W$ was constructed (Fig. 4). Data for a NaOH-treated foil, shown previously to contain voids in the metal at or near the oxide-metal interface, are shown along with those of phosphoric acid-treated foils. For all foils, at least some of the $S$-$W$ points fall along straight line trajectories linking vertices. The end points of the straight-line segments correspond to phases or defects having particular $S$ and $W$ parameters. Those in Fig. 4 represent bulk defect-free aluminum ($S = 1.00$, $W = 1.00$), surface oxide ($S = 0.94$, $W = 1.5$), and an open volume defect ($S = 1.08$, $W = 0.74$). This defect clearly has the same $S$ and $W$ parameters as the void formed by caustic treatment, a strong indication that it is also a void. Straight lines in a $S$-$W$ plot imply that only the defects or phases at the end points contribute to annihilation. Both straight segments in Fig. 4 connect to the $S$ and $W$ parameters of the void. Since data for all the samples fall on these segments, this void is the predominant defect type found on each sample, including the foils without prominent peaks in their $S$-energy profiles (e.g., treatments shorter than 23 s in Fig. 2). The voids in the latter foils were apparently masked by the low-$S$ oxide layer. Because the extensive dissolution during electropolishing would have removed any pre-existing defects, these voids very likely formed as a result of polishing. In all foils, the high $S$ parameter of the void indicates that it is at least 1 nm in size, and that at least part of its surface is metallic and oxide-free. As pointed out earlier, the latter attribute suggests that the void surface should be highly reactive upon exposure, should the covering material be removed by dissolution. Further, the metallic surface of the voids indicates that they either lie along the interface, or else within the metal beneath the oxide film.

Recently, TEM studies of rolled aluminum alloys have revealed 2-8 μm thick, subsurface “active layers,” which promote filiform corrosion. The active layers are characterized by very small grains 50-200 nm in size, and also the presence of precipitated intermetallics. While such layers may contain defects, their presence in the foils of this work is considered unlikely, since the minimum impurity content needed for an active layer appears to be about 0.2%, an order of magnitude larger than that of the present foil.
Also, as mentioned in the Experimental section, capacitor foils are composed of 100 μm size grains spanning the entire foil thickness, so nanocrystalline subsurface layers are improbable.

Simulation of positron measurements.—Quantitative information about the concentration and depth distribution of voids was obtained by simulation of the positron measurements, based on the positron diffusion-annihilation equation.\(^2\)\(^3\)\(^4\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\) These simulations are necessary to correct the measured \(S\) in the defect layer for the effects of variable implantation depth at a given beam energy, as well as diffusion of implanted positrons out of the layer. Either of these effects would lead to a decrease of the measured \(S\) in the defect layer below its true value, because the oxide and bulk aluminum adjacent to the defect layer have relatively smaller \(S\) parameters. The simulations also yielded the thickness of the defect and oxide layers.

The data in Fig. 1 and 2 were simulated using the VEPFIT software application,\(^1\)\(^8\)\(^9\) and the resulting model \(S\)-energy curves are shown as solid lines. Simulations of caustic-treated foils were carried out by Hebert et al.,\(^3\) in which the samples were depicted by a simple two-layer model consisting of a surface-adjacent defect layer and bulk aluminum, with the oxide film factored into the surface boundary condition. In the present work, a three-layer model was instead used which explicitly included the surface oxide, in addition to the defect layer and bulk aluminum. This approach allowed the oxide thickness to be obtained and compared to capacitance measurements. Each layer was characterized by its thickness, characteristic \(S\) value, and positron diffusion length. The diffusion length is the mean distance positrons can diffuse prior to annihilation or trapping into defects. The bulk and oxide layer diffusion lengths were set according to values from the literature, at 150\(^1\)\(^8\)\(^9\)\(^10\)\(^11\)\(^12\) and 20 nm,\(^2\)\(^13\) respectively. The oxide \(S\) parameter was determined to be 0.92, through measurements of aluminum samples with anodically grown oxides, for which the oxide film appeared as a plateau in the \(S\)-energy profile.\(^12\)\(^13\)\(^14\)\(^15\) The defect layer was assumed to have a large void concentration, and its diffusion length was set to the small value of 1 nm. Values close to 1 nm had been obtained using the two-layer model in which the diffusion length was a free parameter.\(^16\)\(^17\)\(^18\) The remaining model parameters adjusted by VEPFIT during fitting were the oxide thickness, defect layer thickness, and the surface, bulk, and defect layer \(S\) parameters. The foils in Fig. 2 with thick porous oxides were not simulated, since VEPFIT would not adequately describe implantation of positrons in the porous oxide layer. The results of the simulations are given in Table I.

The phosphoric acid treatment itself caused the defect layer \(S\) parameter \(S_d\) to increase substantially, from 1.034 for the as-received foil to 1.075, and the combination of electropolishing and \(\text{H}_3\text{PO}_4\) treatment resulted in a value of 1.058. Similar increases of \(S_d\) were found after the \(\text{NaOH}\) treatment and were attributed to higher void volume fractions in the defect layer.\(^3\) However, recent Auger spectroscopy and AFM results revealed the presence on the as-received foil of 100 nm scale hill-like areas with a relatively thicker oxide film.\(^4\) Because of the nonuniform film thickness, oxide may be found at depths within the model defect layer. Thus, on the as-received foil, \(S_d\) may be influenced by the volume fractions of both void \((f_d)\) and oxide \((f_{\text{ox}})\) in the defect layer. That is, \(S_d = \frac{1}{S_{\text{ox}}} f_{\text{ox}} S_{\text{ox}} + (1 - f_{\text{ox}} - f_d) S_b\), where \(S_{\text{D}}, S_{\text{ox}},\) and \(S_b(=1.0)\) are the \(S\) parameters of the voids’ oxide and aluminum crystal within the defect layer. Since \(S_{\text{ax}}\) is smaller than 1.0, the increase of \(S_d\) due to phosphoric acid treatment may be due either to a larger void volume fraction or to removal of the oxide “hills” by dissolution in the acid. For this reason, it cannot be said with certainty whether the \(\text{H}_3\text{PO}_4\) treatment produces an overall enhancement of the void volume fraction. On the other hand, the larger \(S_d\) obtained by treatment of unpolished \(\text{V}_{\text{a}}\) electropolished foil indicates that the former sample had a higher void volume fraction than the latter. Table I lists the fitting results of a foil electropolished in theJacquet bath in which no thick oxide is formed. The \(S_d\) value of 1.050 indicates that interfacial voids are present on this sample, despite the dissolution of the surface layer containing the voids in the as-received foil. This result can be taken as further evidence that voids are formed by electropolishing.

The treatments also affect the defect layer and oxide thickness. These measurements are discussed further in the next two sections with regard to the AFM and capacitance measurements. According to Table I, the defect layer thickness is 118 nm in the as-received foil, compared with 20-50 nm after \(\text{H}_3\text{PO}_4\) treatment. The dissolution rate in phosphoric acid was measured and found to be 120 nm/min. The initial defect layer would then have dissolved during the 1 min treatment of unpolished foil, and would certainly have done so during electropolishing. It is clear that the defect layer after the treatment is dominated by new defects introduced by the acid immersion or electropolishing. Thus, while the overall void concentration may not be increased by the \(\text{H}_3\text{PO}_4\) treatment, the voids may be redistributed on the surface.

In summary, the PAS measurements indicate that both phosphoric acid treatment and electropolishing result in the formation of new interfacial voids, replacing those found in the as-received foil.

### Table I. Defect layer parameters from simulation of positron measurements.

<table>
<thead>
<tr>
<th>Phosphoric acid treatment time</th>
<th>Defect layer (S) parameter</th>
<th>Oxide layer thickness (nm)</th>
<th>Defect layer thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT(^a)</td>
<td>1.034</td>
<td>3.9</td>
<td>118</td>
</tr>
<tr>
<td>5 s</td>
<td>1.070</td>
<td>2.1</td>
<td>34</td>
</tr>
<tr>
<td>1 min</td>
<td>1.075</td>
<td>0.36</td>
<td>44</td>
</tr>
<tr>
<td>23 s (EP)(^b)</td>
<td>1.045</td>
<td>3.5</td>
<td>52</td>
</tr>
<tr>
<td>27 s (EP)</td>
<td>1.055</td>
<td>1.4</td>
<td>40</td>
</tr>
<tr>
<td>40 s (EP)</td>
<td>1.058</td>
<td>2.0</td>
<td>30</td>
</tr>
<tr>
<td>60 s (EP)</td>
<td>1.057</td>
<td>0.29</td>
<td>24</td>
</tr>
<tr>
<td>NaOH 5 min, NT</td>
<td>1.064</td>
<td>1.4</td>
<td>29</td>
</tr>
<tr>
<td>EP (Jacquet bath), NT</td>
<td>1.050</td>
<td>2.9</td>
<td>38</td>
</tr>
</tbody>
</table>

\(^a\) NT denotes no phosphoric acid treatment.

\(^b\) EP indicates foil was electropolished prior to any phosphoric acid treatment.

Figure 5. Top-view AFM images of foil surfaces: (a) as-received foil (height range of gray scale 90 nm), (b) unpolished foil treated in phosphoric acid for 5 s (height range 149 nm), and (c) electropolished foil treated in phosphoric acid for 60 s (height range 36 nm).
The voids are at least 1 nm in size, have oxide-free metallic surfaces, and lie either along the metal-oxide interface or below it in the metal. Voids at the interface could agglomerate by interfacial diffusion of vacancies formed by oxidation; voids below the interface might nucleate from vacancies injected by oxidation which then diffuse into the metal along dislocations. The oxide-free surfaces of voids suggest that they should be reactive upon exposure to the etchant solution and may function as pit initiation sites. The size, depth, and reactivity of the voids formed during the electropolishing and H₃PO₄ treatments appear to be similar to those previously found after caustic treatment. The results are inconclusive as to whether treating the unpolished foil increases the void volume fractions in the defect layer; however, after treatment the electropolished foil appears to have a smaller void fraction than the unpolished foil. In contrast, the NaOH treatment was found to result in an increased void volume.

*AFM images.*—Visual evidence for the voids detected by positron measurements was sought from AFM images. Foils were immersed in CrO₃-H₃PO₄ baths for various times to dissolve the oxide film and possibly expose the interfacial region containing voids. After immersion in this oxide stripping bath for 1 h, the weight loss was less than the balance sensitivity of about 0.1 mg/cm², suggesting that the stripping treatment may have the ability to remove the oxide layer without dissolving metal. However, it was impossible to detect weight loss equivalent to 10-100 nm thick layers of metal, and so dissolution within the defective regions cannot be precluded.

Figure 5 presents images of aluminum surfaces prior to immersion in the oxide stripping solution. The images are of as-received foil, unpolished foil after 5 s phosphoric acid treatment, and electropolished foil after H₃PO₄ treatment. The ridges on the first two types of surfaces are produced by the rolling operation during fabrication of the foils. The electropolished foil is covered with 100-200 nm wide particles. This granular topography is that of the top surface of a porous oxide layer left by electropolishing; such a layer is consistent with the positron measurements in Fig. 3. None of the images in Fig. 5 contain open cavities, nor could cavities be found on any foils not subjected to the oxide stripping treatment.

![Figure 6](image-url)
Images after immersion in the oxide stripping bath are shown in Fig. 6. After stripping for times of about 1 min, open cavities appear in the images of both as-received and unpolished phosphoric acid-treated foils. Some of the cavities on the as-received foil in the images of both as-received and unpolished phosphoric acid-treatment time.

The effect of stripping on the electropolished foil is more complex and depends on the phosphoric acid treatment time. For example, in the case of the 35 s H₃PO₄ treatment, the topography remained similar to that in Fig. 5 for stripping times up to 180 s. At 190 s, the roughness decreased dramatically and the surface was covered with a mosaic pattern composed of hills about 10 nm high and 60-100 nm wide (Fig. 6c). This texture is similar to that reported earlier after electropolishing aluminum in a different bath and represents the electropolished aluminum surface after dissolution of the porous oxide overlayer. After further stripping up to 240 s, the topography remained the same, but at 250 s, a large number of open cavities were found, which appeared to be randomly distributed on the surface (Fig. 6d). These cavities are similar in size to those in Fig. 6b. A similar topographic evolution during stripping occurred for other H₃PO₄ treatment times, but the time to dissolve the porous oxide was extended when the phosphoric acid treatment was shorter. The estimated number density of cavities was 10⁶ to 10⁷ cm⁻² on both as-received and treated foils.

AFM was used to measure the depths of cavities for comparison with the defect layer thickness derived from positron measurements. The results are shown in Fig. 7, in which the plotted depths are averages of roughly 50 cavities. As in the case of caustic treatment, there is close agreement between the mean cavity depth and the defect layer thickness, for both unpolished and electropolished foil. The agreement between the PAS and AFM measurements supports the idea that the cavities originate from interfacial voids which are exposed at the surface in the oxide stripping bath. However, since some dissolution from cavities may occur in this bath, the geometric details of voids should not be inferred directly from the images of cavities. For example, cavities may originate at sites where clusters of nanometer-scale voids span the thickness of the defect layer. After exposure of the top layer of voids, further dissolution would link the voids in the cluster, giving it the appearance of a single cavity.

**Capacitance measurements.**—Changes in the surface oxide layer thickness resulting from the H₃PO₄ treatment were characterized for comparison with the PAS simulations and to help explain the effect of the treatment on etching. The oxide thickness was determined from measurements of the interfacial capacitance, which, as described in the Experimental section, was found from the initial slopes of potential transients during anodizing at constant current. The capacitance was assumed to be dominated by that of the non-porous “barrier” oxide layer adjacent to the metal surface. The barrier-layer thickness was determined by dividing the capacitance into the oxide dielectric constant, the value of which was taken to be 9.24. The application of such a parallel-plate capacitor model to alumina films of a few nanometers thickness is supported by earlier measurements of capacitance and film thickness.24-25 The dielectric constant deduced from these results compares favorably with that of anodic alumina films. The oxide thickness found in this way is plotted in Fig. 8, along with the thickness from the PAS simulation. For the unpolished foil, the capacitance-derived oxide thickness was initially 4 nm and decreased to a steady-state value of 2 nm after 20 s H₃PO₄ treatment. For electropolished foil, the thickness from the capacitance was at first 24 nm and decreased monotonically to the same steady-state value of 2 nm at 40 s.

The capacitance measurements then reveal a significant loss of oxide thickness due to phosphoric acid treatment. Especially for the unpolished foil, Fig. 8 demonstrates good semiquantitative agreement with the oxide thickness obtained from the PAS simulations, giving additional support to the defect layer characteristics derived from VEPFIT. Numerical discrepancies between PAS- and capacitance-derived thickness may be due to deviations of the defect layer and oxide diffusion lengths from their assumed values. For example, the low oxide thickness of about 0.3 nm after 1 min treatments may be due to a defect layer positron diffusion length which is smaller than the assumed value of 1 nm, or to a large number of defects in the oxide film. Figure 8 indicates that the energy at the maximum S in Fig. 1 and 2 is determined by the oxide thickness and not by the defect layer diffusion length as indicated earlier. The diffusion lengths reported in Ref. 3 may be taken as approximately equivalent to oxide thickness.

**Anodic etching after phosphoric acid treatment.**—To demonstrate the effect of H₃PO₄ treatment on etching, as-received and electropolished foils were treated in the phosphoric acid bath and then anodically etched for 100 ms at either constant potential or current. Potentiostatic etching was carried out in 1 M HCl at 70°C and an applied potential of −0.35 V. SEM images of the resulting etched surfaces are shown in Fig. 9a-c. Only a few isolated pits were
found on the as-received foil (Fig. 9a). On both phosphoric acid-treated foils (Fig. 9b and c), the pits are approximately square in shape with widths up to 2 \( \mu \text{m} \), and their number densities are similar to one another and much larger than that on the as-received sample. The sides of nearby pits are aligned as expected for crystallographic etching. Many of the pits in Fig. 9b are distributed along the small ridges noted earlier. Pits in Fig. 9c appear to be randomly distributed, but clusters possibly associated with individual grains can be identified.

The surface of another as-received foil, etched at a constant current density of 0.20 A/cm\(^2\), is shown in Fig. 9d. The size and distribution of pits along ridges is similar to that in Fig. 9b, and the number of pits is clearly much larger than that formed by potentiostatic etching in Fig. 9a.

The pit number density at 100 ms was determined from SEM images which were taken at five random locations for each etched surface, with different magnifications ranging from 200 to 1000. This sampling procedure was intended to enhance the statistical reliability of the pit density data. The results are shown in Fig. 10. The pit number density on the as-received foil was found to be approximately \( 6 \times 10^3 \) cm\(^{-2}\), and the 1 min H\(_3\)PO\(_4\) treatment increased the number density by about two orders of magnitude, to \( 3 \times 10^5 \) cm\(^{-2}\). On the other hand, the number density on the as-received foil etched at constant current was estimated to be on the order of \( 10^7 \) cm\(^{-2}\), even larger than that obtained by etching treated foils at constant potential. The effect of phosphoric acid treatment on electropolished foils strongly depends on the treatment time. For treatment times up to 25 s, essentially no pits were found after anodic etching. However, as the treatment time was increased to 40 s, the pit density increased to at least \( 10^5 \) cm\(^{-2}\), similar to the highest value for the unpolished foil after phosphoric acid treatment.

Examples of electrochemical transients during etching of unpolished foils are shown in Fig. 11. The current during potentiostatic etching after treatment reaches values close to 0.2 A/cm\(^2\) during the 100 ms period used for SEM observations, while that on the as-received foil remains very small. However, after further etching for 5 s it rises to about 60 mA/cm\(^2\). These transients confirm that for etching at \(-0.35\) V, the rate of pit initiation is substantially increased by H\(_3\)PO\(_4\) treatment. The potential transient during constant-current etching of the as-received foil shows that the high rate of pitting found in Fig. 9d is accompanied by a potential as high as 0 V.

**Figure 9.** SEMs of aluminum foils after anodic etching in 1 M HCl at 70°C for 100 ms: (a) as-received foil etched at \(-0.35\) V, (b) unpolished foil treated in phosphoric acid for 1 min, etched as (a), (c) electropolished foil phosphoric acid treated for 1 min, etched as (a), and (d) as-received foil etched at 0.20 A/cm\(^2\).
Factors influencing pit initiation.—The morphologies of surfaces with cavities or etch pits can be compared to assess whether voids might function as pit initiation sites. Such a comparison is reasonable, since interfacial voids revealed during etching would likely grow by dissolution in the same fashion as the cavities exposed at the surface by the oxide stripping solution. While etch pits are about an order of magnitude larger in size than cavities, this difference would likely result from a much larger extent of dissolution from pits relative to that in the passivating CrO$_3$-H$_3$PO$_4$ stripping bath. Slow cavity growth in this bath was noted previously in AFM images after long stripping times.$^3$ Despite the much larger pits found in the present experiments, the sizes of etch pits and cavities are comparable when the time of anodic current application is only a few milliseconds, so that the extent of dissolution from pits is limited.$^{39}$ In Ref. 29, the pit volume was found to be of the order of ten times larger than the equivalent of the faradaic charge. The excess volume above that due to anodic dissolution is consistent with the origin of the pit at a pre-existing void or cluster of voids.

Aside from pit and cavity size, several other geometric aspects of both structures are similar. The cross-sectional shapes of pits and cavities are comparable in that both exhibit similar length and width dimensions. The distributions of both structures on the surface also share common features. On the unpolished treated and as-received foils, pits and cavities are found preferentially along the ridges associated with rolling. On the H$_3$PO$_4$-treated electropolished foils, both appear to be randomly distributed over the surface. Finally, it is significant that the number density of cavities (10$^7$ cm$^{-2}$ on treated and untreated unpolished foil, and 10$^6$ to 10$^7$ cm$^{-2}$ on treated electropolished foil) is of the same order of magnitude as the highest number density of pits that is typically found during anodic etching.$^4$

Other types of surface defects which might be considered as candidate pitting sites, such as dislocations and grain boundaries, have very different number densities from those of pits.

The favorable comparison of cavity and pit morphology, distribution, and number is taken as support for the idea that interfacial voids function as pitting sites. Evidence linking voids and pits was also found in the study of the caustic pretreatment.$^3$ As already mentioned, it is especially compelling in this regard that voids are clearly identified by the nondestructive PAS measurements, which also show that their surfaces are oxide-free and therefore reactive. This observation provides a reasonable mechanism for voids to become pits. Neither the PAS nor AFM results show that the overall number of voids is enhanced by the phosphoric acid treatment.

While voids may define pitting sites, the rate of pit initiation on a given surface was shown here to strongly depend on the oxide thickness and potential. In potentiostatic etching at −0.35 V, pit number densities exceeding 10$^5$ cm$^{-2}$ are obtained only when the phosphoric acid treatment has reduced the oxide thickness to about 2 nm. This is especially clear in the case of the electropolished foil, when the trends of oxide thickness (Fig. 8) and pit number density (Fig. 10) are compared as a function of treatment time. In particular, very few pits form after 23 s treatment, where capacitance measurement of film thickness is 6 nm, even though PAS shows the presence of interfacial voids. For the unpolished foil, very few pits initiate at −0.35 V without treatment when the oxide thickness is 4 nm. However, this inhibition by the relatively thick oxide is overcome in galvanostatic etching experiments for which the potential is more positive then −0.35 V. This implies that the low pit density of this foil in potentiostatic etching is not caused by a lack of pitting sites. Instead, the rate of pit initiation on any given sample is apparently enhanced by high potentials and small oxide thicknesses, suggesting that the electric field across the oxide layer may control the rate of the process through which voids become pits.

A mechanism for etch pit initiation can be put forward which explains the dual importance of interfacial voids and the electric field in the oxide. Pits would be expected to initiate at interfacial voids when the top surface of the void is brought into contact with the metal-film interface, by oxidation of the layer of metal between the top surface of the void and the oxide film. The unsupported oxide would then dissolve or collapse on top of the void, exposing its reactive oxide-free internal surface, and locally rapid metal dissolution would ensue. During the etching experiment, metal atoms are uniformly oxidized on the unpitted surface, and as a result the metal-oxide interface on this surface recedes toward the bulk metal. The rate of this oxidation process is influenced by that of ionic conduction through the film, which is a function of the electric field in the oxide.$^{24,30}$ For a given distribution of subsurface voids, the electric field therefore affects the velocity with which the metal-film interface moves in the direction of the bulk metal, and thus the rate of exposure of subsurface voids. High fields in the oxide would accelerate the motion of the metal-film interface and cause voids in the defect layer to be exposed at a large rate.

Figure 10. Pit number density after etching aluminum foils, showing effect of phosphoric acid treatment time on both (●, ■, ▲) unpolished foils and (○, □, △, ▲) electropolished foils. Etching was carried out at −0.35 V for 100 ms in 1 M HCl at 70°C.

Figure 11. Electrochemical transients during etching of unpolished foils: current transients for as-received foil and H$_3$PO$_4$-treated foil, and potential transient for as-received foil. Etching conditions are those in Fig. 8a, b, and d, except that the period of potentiostatic etching for the as-received foil was extended to 5 s. Potential was corrected for the cell ohmic potential drop.
Conclusions

The effect of phosphoric acid immersion as a pretreatment for anodic etching of aluminum was explored. PAS measurements indicated that the pretreatment formed metallic voids, replacing those present in the as-received foils. The voids were located either at the metal-oxide interface, or below it at depths up to about 100 nm. The high S parameter of the voids showed their surfaces to be free of oxide, implying that they should be reactive if exposed at the surface during etching. AFM images of foils with chemically stripped oxide layers showed the presence of cavities whose depth agreed with the thickness of the subsurface defect layer identified by PAS. The cavities are then likely to be closely related to the interfacial voids. Capacitance measurements indicated that the treatment caused the oxide layer thickness to decrease to about 2 nm. The film thickness obtained in this way also agreed with that derived from PAS. According to SEM images after anodic etching, cavities and etch pits have similar distributions and shapes; also, the maximum number of pits formed by etching (about $10^7 \text{ cm}^{-2}$) is the same as the estimated cavity number density. These results support the idea that pits initiate at interfacial voids when the covering material is dissolved during the etching experiment. The rate of pit initiation at these sites was shown to be increased at high potentials and small oxide thickness, suggesting that the electric field in the film may control the rate of pitting. In fact, oxide thickness reduction may be the most important reason for the enhancement of the pit number by the phosphoric acid treatment. It is noted that the present model of pit initiation, in which uniform dissolution exposes pre-existing voids below the oxide, differs from the point defect model of Macdonald, where local accumulation of vacancies within the oxide leads to its breakdown.31

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