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Interfacial Void Model for Corrosion Pit Initiation on Aluminum

Kamal Muthukrishnan, Kurt R. Hebert, and Takeshi Makino

A model for pit initiation during galvanostatic anodic etching of aluminum in acid chloride-containing solutions was developed. The predictions were compared to experimental potential transients and pit-size distributions. The model presumed that pits initiated from subsurface nanoscale voids, which were exposed by uniform corrosion. Void concentrations fit from potential transients depended on times of caustic and acid exposure before etching, in agreement with prior characterization of the voids by positron annihilation measurements. The model yielded realistic predictions of the effect of applied current density and temperature on the transient. The effective void concentration was found to increase with the chloride concentration in the etching solution; this suggested that higher chloride concentrations inhibit passivation of newly exposed voids, enhancing their survival probability. On the whole, the interfacial void model provided a promising quantitative description of pit initiation during anodic etching.

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In the fabrication of electrolytic capacitors, aluminum foils are anodically etched in hot chloride solutions.1 Etching produces \(10^5-10^7 \text{ cm}^{-2}\) micrometer-scale corrosion pits, and thereby enhances the foil surface area. The ability to control both the pit number density and the distribution of pit sites would be of considerable technological interest. Since pit formation during etching and corrosion are fundamentally similar, insight would also be gained into the broader fundamental problem of passivity breakdown and pit initiation on metals.2-4 Effective control of pitting of metals requires identifying surface sites favoring pit formation; in recent years, several new experimental methods have been applied to this problem. Scanning electrochemical microscopy (SECM) demonstrated pit formation in titanium at electroactive areas of \(\sim 10 \mu \text{m}^2\).5,6 On aluminum, SECM identified micrometer scale electronically conductive sites in the surface oxide film.7,8 Maurice et al. found evidence with scanning tunneling microscopy that metastable pits on nickel corresponded to grain boundaries in the passive oxide film.9 Using a microcapillary cell, Suter and Böhn found that the number of metastable pits on stainless steels correlated with 10-200 ppm levels of bulk sulfur.10,11

The nature of pit initiation sites on foils used for anodic etching was previously investigated by positron annihilation spectroscopy (PAS),12-14 PAS revealed nanometer scale voids in aluminum foils, which had oxide-free metallic surfaces and were positioned within 10-100 nm of the metal-oxide film interface. These buried voids were present in as-annealed foils, and were formed by dissolution in NaOH, a treatment which is used to enhance the rate of pitting during subsequent etching. AFM images of surfaces with chemically stripped oxide films revealed open cavities, the depth and area coverage of which agreed with statistics derived from PAS.12,13 The morphology and surface distribution of these cavities resembled those of pits formed by anodic etching, indicating a correspondence between locations of voids and pit sites. It was proposed that pits initiate when uniform corrosion removes the material overlying voids, exposing their reactive oxide-free surfaces. The number of pits was generally smaller than that of cavities revealed by oxide stripping, but approached the cavity number density when the etching conditions were particularly aggressive.13 Thus, in general some fraction of the voids may passivate upon exposure and fail to become pits.

The hypothesis that pits initiate from interfacial voids suggests that the rate of pitting should increase with that of uniform corrosion. Supporting this notion, the formation of large numbers of etch pits was found to be favored by factors which accelerate uniform corrosion.15 Interestingly, the rate of pit initiation on stainless steel was observed to increase with that of uniform corrosion, for a wide range of experimental conditions.15 In the present study, a mathematical model for pit initiation during anodic etching of aluminum was developed. The model is based on the interfacial void hypothesis; that is, the rate of pit formation is proportional to the interfacial void concentration and the uniform corrosion rate. Electrochemical potential transients during the early stages of anodic etching were predicted, as well as pit size distributions and initiation rates. The simulation was tested by comparison to experiments exploring effects of several different etching parameters: NaOH treatment time, applied current density, temperature, open-circuit exposure time in the etching bath, chloride concentration, and bath circulation. The goal was to determine whether etching behavior is consistent with the hypothesis that interfacial voids are the primary pitting site.

Mathematical Model

The model is based on a current balance pertaining to times within 100-200 ms after the initial application of current. At these times, submicrometer etch pits are the predominant type of corrosion structure, and the etch tunnels which are found at later times have not yet appeared. The current balance includes terms for capacitive charging current, current from uniform corrosion on the oxide-covered surface \((i_u)\), and dissolution current from pits \((i_{pit})\).

\[
i_{app} = C_d \frac{dE}{dt} + i_u + i_{pa}
\]

\[
i_{pit} \text{ includes contributions from all pits nucleated at all times up to the current time } t
\]

\[
i_{pa} = 2 \pi r_0^2 j_a \int_0^t \left[ 1 + \frac{v_d}{v_0} (t - \tau) \right]^2 \left( \frac{dN_{pa}}{dt}\right) d\tau
\]

In Eq. 2, the pits are hemispherical and dissolve at a constant current density \(i_a\). Pits are assumed to have uniform depth \(r_0\) when they first appear. The factor in brackets accounts for pit growth since nucleation. \(dN_{pa}/d\tau\) is the nucleation rate, and so \((dN_{pa}/d\tau)d\tau\) represents the number of pits nucleated in time interval \(d\tau\). Oxide film passivation within pits is assumed not to occur, since during the time of interest the potential is much more anodic than the critical potential for repassivation, \(E_R\). The current density through the intact oxide film \(i_a\) obeys high-field conduction kinetics19,20

\[
i_a = i_{a0} \exp \left( \frac{B\phi}{\delta} \right)
\]

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where the potential drop through the oxide $\phi = E - iR_a - E_{Al|Al_2O_3}$, $i_a$ accounts for both film growth and dissolution of metal ions through the film. The film thickness $\delta$ is determined by

$$\frac{d\delta}{dt} = \frac{i_e}{F C_{\text{al}}},$$

where the current efficiency $e$ is the fraction of $i_a$ resulting in film growth as opposed to $\text{Al}^{+3}$ dissolution.

As a result of the consumption of metal by uniform corrosion, the metal-film interface moves in the direction toward the bulk metal. According to the void hypothesis, a pit initiates when this interface contacts a void buried in the metal beneath the film. The thin oxide layer over a void would likely be mechanically unstable due to the pressure difference of 1 atm across the film, and chemically unstable because of the tendency of alumina to dissolve in the acidic etchant solution. Assuming a uniform buried void concentration $C_V$, the pit nucleation rate is

$$\frac{dN_{\text{pit}}}{dt} = \left( \frac{i_a}{3F C_{\text{al}}} \right) C_V$$

where the factor in parentheses is the velocity of the metal-film interface. Presumably, any voids at depths of several nanometers below the oxide-metal interface would have formed by dislocation-enhanced diffusion of vacancies formed by metal atom oxidation. The location of voids at such depths is not precluded by the PAS results.

Equations 1-5 were solved to determine the potential transient $E(t)$ and the pit number density $N_{\text{pit}}(t)$. A Fortran program was written to numerically integrate the system of two ordinary differential equations (Eq. 1 and 4), along with an integral equation (Eq. 2), using subroutines from the IMSL library (Visual Numerics). The dependent variables were $\phi$ and $i_a$; the initial condition for $\delta$ was chosen as described below in the Results section. The simulation was insensitive to the initial value of $\phi$, which was set to zero. At very early times, the current was entirely capacitive (Eq. 1), but $\phi$ rapidly approached a value at which uniform corrosion supplied the applied current. $r_{\text{min}}(t)$, the root-mean-square pit radius, was calculated for comparison with SEM measurements of pit size distributions. $r_{\text{min}}$ was obtained from $N_{\text{pit}}(t)$

$$\left( \frac{r_{\text{min}}}{r_0} \right)^2 = \frac{1}{N_{\text{pit}}(t)} \int_0^t \left( 1 + \frac{v_d}{r_0} (t - \tau) \right) \left( \frac{dN_{\text{pit}}(t)}{dt} \right) d\tau.$$

Results of model calculations are presented below along with the experimental results.

**Experimental**

The aluminum foils used for etching experiments were 99.99% purity and 100 $\mu$m thick (Toyo). Extensive annealing resulted in a large grain size of approximately 100 $\mu$m. Etching was carried out in aqueous solutions containing mixtures of HCl and H$_2$SO$_4$, at a constant applied current density and at temperatures from 70 to 90°C. Procedures for etching experiments were the same as those discussed in Ref. 16. Parallel experiments were also conducted in solutions containing only H$_2$SO$_4$, to help characterize uniform oxide growth and dissolution processes during etching. Prior to etching, foils were pretreated by immersion for various times in aqueous 1 M NaOH solution, at open circuit and room temperature. In the normal procedure used in etching experiments, the bath was circulated using a magnetic stirring bar, and the applied current was initiated 10 s after immersion of foils in the etchant bath. A potentiostat-galvanostat (EG&G PAR 273) was used to apply a constant current between the aluminum foil and a Pt wire counter electrode. During etching, the potential of the aluminum foil vs. a Ag/AgCl/4 M KCl reference electrode was recorded with a high speed voltmeter (Keithley 194A) interfaced to a computer. Foils were examined by scanning electron microscopy (SEM) to reveal the morphology and size distributions of etch pits.

**Results and Discussion**

**Effect of NaOH pretreatment time on pit initiation.—** Potential transients with characteristic maxima were observed during the initial phase of etching, similar to those reported earlier.16-18 Figure 1 shows examples of transients in 1 M HCl-3 M H$_2$SO$_4$ etchant at 70°C and 0.2 A/cm², for various pretreatment times in NaOH. After a rapid increase in the first millisecond due to capacitive charging, the potential rose to a maximum at a slower, approximately constant rate, and then rapidly decreased to a final constant value. This final potential has been identified as the repassivation potential, below which the dissolving surfaces of pits are passivated by oxide.21 The dashed lines in Fig. 1 are potential transients in 3 M H$_2$SO$_4$ solution, with otherwise the same experimental conditions as the etching experiments. For the equivalent pretreatment times, the transients in HCl-H$_2$SO$_4$ and H$_2$SO$_4$ are the same up to times near the potential maximum in HCl-H$_2$SO$_4$. Since only anodic oxide growth and uniform dissolution occurred in the H$_2$SO$_4$ solution, these uniform corrosion processes were apparently also the predominant current sources in HCl-H$_2$SO$_4$, at times when the two transients coincided.

Despite the importance of uniform corrosion current before the potential maximum, pits were evident in SEM images.16 The rapid potential decrease occurred when the overall pitting current had increased to levels approaching the applied current.16,17 The time of this decrease is therefore an inverse measure of the pit nucleation rate, and is denoted by $t_{\text{pit}}$. The effect of NaOH treatment time on the potential transients is illustrated in Fig. 2 (solid lines). $t_{\text{pit}}$ decreased as the NaOH time was increased from 0 to 1 min, and then increased for treatment times up to 20 min. Evidently, the pit initiation rate increased up to 1 min pretreatment time, and then decreased.

The potential transients in Fig. 2 were modeled using the simulation. In the calculations, the void radius $r_0$ was set to 50 nm. This was the minimum pit depth observed by SEM after application of pulses of etching current of a few milliseconds duration. $r_0$ should reflect growth of buried voids by solid-state diffusion, and may also include growth by dissolution for a brief period after voids are exposed. This rapid initial dissolution has been noted earlier,17 and may precede the establishment of a steady-state chloride layer on the void surface.16 The effect of different assumed values of $r_0$ is considered below. High-field conduction kinetic parameters $i_{\text{ag}}$ and $B$ at
70°C were taken from measurements by Harkness and Young,\textsuperscript{19} and the dissolution current density $i_d$ was set to the constant value of 6.1 A/cm\textsuperscript{2}. These parameters were experimentally verified in Ref. 16. The initial film thickness, $d_0$, and current efficiency for oxide growth, $e$, were fit from the potential transient from the parallel experiment in H\textsubscript{2}SO\textsubscript{4} (Fig. 1). $d_0$ was determined from the initial potential and $e$ from the slope of the linear potential rise. The model parameters used in the simulations are summarized in Table I.

The model potential transients in Fig. 2 (dashed lines) were obtained from fitting $C_v$ to the experimental transients, leaving all other parameters at their independently determined values. It is evident that the simulation reproduced the experimental transients very well. The final constant potential is not predicted, since the model does not include passivation. The fit values of $C_v$ are plotted in Fig. 3, along with the defect layer $S$ parameter ($S_d$) from PAS.\textsuperscript{12} Variations of $S_d$ are due to changes of the void volume fraction in the defect layer, which in the model is proportional to $C_v$. When $r_0$ was set to 0.5 or 5 nm, the model fit the transients equally well with the value of 50 nm. The $C_v$ values obtained for these smaller assumed void sizes are also shown in Fig. 3. Figure 3 shows that independent of $r_0$, $S_d$ and $C_v$ have similar dependencies on pretreatment time, both with maxima at about 1 min. Thus, the dependence of $C_v$ on pretreatment time, as inferred from the potential transients, parallels that of the PAS measurements of subsurface voids. This result is consistent with the hypothesis that interfacial voids are the predominant pit initiation sites.

**Effect of applied current density on pit initiation.**—After the value of $C_v$ was set at a given pretreatment time, all model parameters were fixed. The simulation was then applied to predict behavior for other applied current densities and temperatures. Figure 4 compares predicted and experimental transients at different applied current densities, in the 1 M HCl-3 M H\textsubscript{2}SO\textsubscript{4} bath at 70°C and with a NaOH treatment time of 30 s. $r_0$ was set to 50 nm, and the corresponding $C_v$ from Fig. 3 was chosen. Figure 4 demonstrates quantitative agreement between the experimental and simulated potential transients. In particular, in both model and experimental transients, $t_{\text{pit}}$ was approximately 80 ms, and did not change appreciably with applied current. This is at first surprising, since the number of pits increases with the applied current.

The reason for the independence of $t_{\text{pit}}$ on $i_{\text{app}}$ are elucidated by examination of the model. As Fig. 1 indicates, the current is dominated by uniform oxidation and corrosion during most of the poten-

### Table I. Summary of model parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>2.99 cm/MV\textsuperscript{19}</td>
</tr>
<tr>
<td>$C_d$</td>
<td>5.0 µF/cm\textsuperscript{22}</td>
</tr>
<tr>
<td>$C_v$</td>
<td>Adjusted (Fig. 3)</td>
</tr>
<tr>
<td>$i_{\mu}$</td>
<td>$1.8 \times 10^{-32}$ A/cm\textsuperscript{19}</td>
</tr>
<tr>
<td>$i_d$</td>
<td>6.1 A/cm\textsuperscript{2} at 70°C, at other temperatures determined by activation energy of 15 kcal/mol\textsuperscript{22}</td>
</tr>
<tr>
<td>$r_0$</td>
<td>0.5-50 nm\textsuperscript{a}</td>
</tr>
<tr>
<td>$\delta_0$</td>
<td>Determined using potential transients in 3 M H\textsubscript{2}SO\textsubscript{4}\textsuperscript{a}</td>
</tr>
<tr>
<td>$e$</td>
<td>Determined using potential transients in 3 M H\textsubscript{2}SO\textsubscript{4}\textsuperscript{a}</td>
</tr>
<tr>
<td>$\phi_0$</td>
<td>0.0 V\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Detailed explanation found in text.
...the decrease of pit initiation rate is determined by the uniform corrosion rate and the pre-existing void concentration.

Effect of temperature on pit initiation.—Figure 5 shows a series of experimental potential transients at temperatures from 70 to 90°C, for the standard pretreatment time of 30 s. The dissolution rate was shown earlier to follow an Arrhenius temperature dependence with an activation energy of 15 kcal/mol, according to which it changes by a factor of three over this temperature range. Therefore, $v_d$ and $i_d$ were assumed to be the main parameters controlling the effect of temperature in the simulation. The effect of temperature was modeled by changing $v_d$ and $i_d$ according to the activation energy of 15 kcal/mol, and leaving all other parameters the same. Again, $r_0$ was 50 nm, and $C_v$ was set to the appropriate value from Fig. 3 for the 30 s pretreatment. It can be seen that the simulation successfully tracks the decrease of $t_{ps}$ as the temperature is increased. In the simulation, the decrease of $t_{ps}$ with temperature is due to the requirement of fewer pits to supply the current, as the temperature and dissolution current density are increased (as demonstrated by Eq. 7, which indicates that $t_{ps}$ is inversely proportional to $v_d$). The agreement with the measured transients in Fig. 5 suggests that this effect controls the temperature response, as opposed to any intrinsic temperature dependence of pit nucleation kinetics. Again, this finding is consistent with the interfacial void hypothesis, in which the pit initiation rate is determined by the uniform corrosion rate and the pre-existing void concentration.

Effect of time on open circuit prior to etching.—Figure 6 shows potential transients (solid lines) from a series of experiments with different immersion times in the etching bath before current application. Increasing this open circuit time from 10 to 40 s caused $t_{ps}$ to decrease significantly from 85 to 7 ms, suggesting that the pit initiation rate increased appreciably. At the largest open circuit times, a series of decaying potential oscillations initiated at $t_{ps}$, before the potential settled to the final constant value. The simulation of these experiments (dashed lines) was based on the premise that interfacial voids were created during the open circuit period. This assumption is supported by the finding that significant numbers of voids form during immersion in hot acid solutions. The model curves were obtained with $r_0$ set to 50 nm, and with $C_v$ adjusted for agreement with the experimental transients. The fit $C_v$ for the open circuit times of 10, 15, 18, 25, and 40 s were 0.49, 1.1, 10, 26, and 75 $\times 10^{14}$ cm$^{-3}$, respectively. PAS measurements in Ref. 13 found a large increase of the defect layer $S$ parameter from 1.034 to 1.075, during a 1 min immersion of similar foils in 5% $\text{H}_2\text{PO}_4$ at 85°C, suggesting that increases of $C_v$ during the open circuit period are reasonable.

### Table II. Measured and predicted pit depths at $t_{ps}$. Etching in 1 M HCl-3 M $\text{H}_2\text{SO}_4$ at 70°C and 0.2 A/cm$^2$, with 30 s NaOH pretreatment.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Experimental $t_{ps}$ (ms)</th>
<th>Experimental $r_{rms}$ (nm)</th>
<th>Predicted $r_{rms}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>84</td>
<td>300</td>
<td>162</td>
</tr>
<tr>
<td>80</td>
<td>39</td>
<td>250</td>
<td>159</td>
</tr>
<tr>
<td>90</td>
<td>16</td>
<td>150</td>
<td>160</td>
</tr>
</tbody>
</table>

Pit size distributions were measured using SEM at 70, 80, and 90°C, at etch times equivalent to $t_{ps}$. The rms pit radius, $r_{rms}$, was determined using these distributions. Table II compares experimental values of $r_{rms}$ with model predictions (Eq. 6). As the temperature is increased from 70 to 90°C, the experimental pit radius decreased from 300 to 150 nm, while the predicted pit radius remained nearly constant at 160 nm. Thus, while the experimental and model pit sizes were comparable, the model did not capture the decrease of $r_{rms}$ with temperature. However, the magnitude of pit sizes in Table II is realistic, which was not the case when $r_0$ was set to 0.5 or 5 nm, in which case the predicted pit sizes were much too small. In the model predictions, the independence of $r_{rms}$ on temperature is consistent with the approximation $i_{app} \sim i_{app}$, which leads to a simplified expression for $r_{rms}$ (see the Appendix for derivation)

$$\frac{r_{rms}^2}{r_0^2} = \frac{r_0}{3v_d^2p} \left(1 + \frac{v_d r_{pit}}{r_0} \right)^3 - 1$$

$r_{rms}$ from this approximate relation was found to agree with the model values in Table II to within 12%. Equation 8 shows that $r_{rms}/r_0$ depends only on the group ($v_d r_{pit}/r_0$), which according to Eq. 7 is a function of $C_v$ and $r_0$. Thus, $r_{rms}$ depends only on $r_0$ and $C_v$, but not temperature, as indicated in Table II.

The experimentally observed decrease of the experimental $r_{rms}$ with temperature must arise from factors not considered explicitly in the model. The results presented in the next section indicate that significant numbers of voids are formed during the open-circuit period in the etchant bath before application of current. If the size of these voids decreases with bath temperature, they could account for the decrease of $r_{rms}$. Also, as mentioned above, there may be a burst of rapid pit growth upon initial exposure of the reactive void surface. The temperature dependence of $r_{rms}$ could be associated with that of this initial dissolution period. Thus, elucidation of the electrochemistry of the initially oxide-free void surface may be necessary for a complete quantitative understanding of pit initiation.
Effect of HCl concentration on pit initiation.—There is evidence that higher chloride concentrations facilitate pit nucleation, during both anodic etching, and at lower potentials. However, the pit initiation rate in the model is determined by the uniform corrosion rate and the void concentration, neither of which would be influenced directly by the chloride concentration. Hence, it was important to determine whether the pit nucleation rate was affected by the etchant HCl concentration. Aluminum samples were etched in a series of solutions consisting of 3 M H$_2$SO$_4$ along with different concentrations of HCl. The potential transients for these experiments (Fig. 7, solid lines) show that $t_{pit}$ decreased strongly with increasing HCl concentration, from 390 ms in 0.5 HCl to about 40 ms in 3 M HCl. The decreased $t_{pit}$ could result from either larger pit initiation rates or higher metal dissolution current densities in pits, as the HCl concentration is raised. Figure 8 shows SEM images of the aluminum surface, after etching in baths containing 0.5, 1, and 3 M HCl, for times approximately equivalent to $t_{pit}$. As the HCl concentration increased, the number of pits was clearly greater. The decrease of pit size with HCl concentration in the figure results, at least in part, from the shorter etch time. The micrographs then suggest that the pit initiation rate increased with the HCl concentration.

Simulations of the potential transients in Fig. 7 were carried out by adjusting $C_v$ to fit the experimental $t_{pit}$, with $i_d$ and $v_d$ held constant. The predicted transients (dashed lines in Fig. 7) were in good agreement with the experimental ones, except for the case of the 0.5 M HCl-containing bath, where the experimental transient had a smaller maximum potential. This deviation seems to be associated with underprediction of the pit nucleation rate at early times during this etching experiment. The fit $C_v$ values for 0.5, 1, and 3 M HCl were $3.9 \times 10^{13}$, $4.9 \times 10^{13}$, and $4.9 \times 10^{13}$, respectively. Figure 9 shows the predicted pit number densities at $t_{pit}$, along with those estimated from SEM images. The experimental and predicted pit densities are seen to be comparable, which is further evidence that the pit initiation rate and not the pit current density is affected by HCl concentration.

As an explanation for the HCl concentration effect, the possibility was considered that the chloride concentration affects the rate of void formation during the open circuit period. Figure 10 shows potential transients from experiments in which the sample was exposed just prior to etching to solutions of different composition. In all cases, the exposures were at 70°C and etching was carried out in a 1 M HCl-3 M H$_2$SO$_4$ bath at this temperature. The open circuit immersions were for 10 s in 1 M HCl-3 M H$_2$SO$_4$; 20 s in 1 M HCl-3 M H$_2$SO$_4$; and 10 s in 3 M HCl-3 M H$_2$SO$_4$, followed immediately by 10 s in 1 M HCl-3 M H$_2$SO$_4$. The difference between the latter two transients was within experimental reproducibility, and is much smaller than the effect of total time on open circuit. Thus, the substitution of 3 M HCl for 1 M HCl during part of the open circuit period had no significant effect on $t_{pit}$. This implies...
that the etchant HCl concentration does not influence the rate of void formation during open circuit corrosion.

Since the effect of chloride concentration on open circuit is not significant, the results suggest that higher HCl concentrations during etching increase the pit nucleation rate. This trend appears to conflict with the interfacial void hypothesis. On the other hand, the ability of the model to describe the effects of NaOH treatment, applied current density, and open circuit immersion time clearly support the hypothesis. Hence, rejection of the interfacial void model on this basis is not reasonable. An explanation for the HCl concentration effect, within the context of the model, is that newly exposed voids are susceptible to passivation, and so only a fraction survive to become pits. The fit $C_v$ values would then reflect only the voids which actually become pits. If the survival probability is enhanced at higher chloride concentrations, the effect of increased chloride concentration would be modeled by the use of a larger $C_v$. The enhanced survival probability may relate to an increased likelihood of chloride adsorption on the newly exposed void surface, which would inhibit oxide passivation. The idea that some voids fail to become pits is consistent with the high void number densities suggested by AFM images after chemically stripping the oxide film, relative to the somewhat smaller numbers of pits formed during anodic etching.\textsuperscript{12,13}

**Effect of stirring on pit initiation.**—In the standard etching procedure, the etchant bath was circulated with a magnetic stirring bar. The effect of bath circulation on the etching potential transients is illustrated in Fig. 11. Stirring did not affect the transients when a NaOH-treated foil was used, but for as-received foil samples, $t_p$ decreased significantly when stirring was applied. An additional experiment using an as-received foil was carried out in which the solution was unstirred during the open circuit period, and then stirring was initiated upon application of current. Figure 11 shows that the resulting potential transient was nearly the same as when the solution was unstirred at all times. Thus, the decrease of $t_p$ was caused by an effect felt during the open circuit period, and not during etching itself. This result is consistent with the interfacial void hypothesis, in that significant void formation has been demonstrated during the open circuit period. It is possible that convection increases the rate of open-circuit dissolution of the as-received foil, and this results in a larger void concentration. Other results have shown that the extent of open-circuit dissolution, rather than the immersion time, controls void formation.\textsuperscript{14} It is possible that the incremental effect of stirring on void formation during open circuit is significant for the as-received, but not the NaOH-treated foil, since the latter sample has a much larger concentration of voids.

**Conclusions**

A mathematical model was developed for pit initiation during the initial moments of constant-current anodic etching of aluminum in HCl-H$_2$SO$_4$ solutions. The simulation was based on the hypothesis that pits initiate from subsurface nanoscale voids. These voids were previously detected by PAS, which also revealed their oxide-free surfaces, suggesting the possibility that they can function as pit sites. In the model, voids are exposed to solution by uniform corrosion, at which point rapid metal dissolution initiates on their reactive surfaces. Potential transients were measured for a range of pretreatment times over which PAS indicated that the void volume fraction varied appreciably. Subsurface void concentrations were determined by fitting the model to these transients, and were found to have the same dependence on pretreatment time as that revealed by PAS.\textsuperscript{12}
After setting the void concentration by fitting to a standard pretreatment time, the model was then used to predict behavior for a variety of etching temperatures and applied current densities. The predicted potential transients compared well with experimental measurements, supporting the void hypothesis of pit initiation. The rate of pit initiation increased significantly with open circuit exposure time during etching. The model indicated that voids were formed during this open circuit period, in agreement with PAS measurements after high-temperature-acid exposures.\textsuperscript{12} The rate of pit initiation also increased with HCl concentration in the etchant. Simulations suggested that the effective void concentration increased with chloride concentration; based on this result, it was suggested that higher chloride concentrations result in the enhanced stability of voids upon exposure. Comparison of the model to pit size distributions pointed to the need for improved understanding of electrochemical reactions on the newly exposed metal surface. On the whole, however, the model yielded realistic quantitative predictions of pit initiation, supporting the interfacial void hypothesis.

Acknowledgments

The contributions of two of the authors (K.M. and K.R.H.) to this work was supported by St. Jude Medical. Aluminum foils were supplied by Nippon Chemi-Con.

Appendix

The derivation of Eq. 7 and 8 are explained in this Appendix. The approximation on which these equations is based states that the applied current prior to $t_{p0}$ is supplied by uniform corrosion, but at $t_{p0}$ it is furnished only by dissolution from pits. Hence in Eq. 2, $t_{p0}$ on the left side may be set to $t_{p0}$. Since $dN_{p0}/dt$ inside the integral applies to times prior to $t_{p0}$, it may be substituted with Eq. 5 in which the uniform corrosion current density $i_{p}$ is set to $i_{app}$. With these substitutions, Eq. 2 becomes

$$\frac{3FC_{Al}}{2\pi d_{f}} = \int_{0}^{\infty} \left[ 1 + \frac{v_{d}}{r_{0}} (t - \tau) \right]^{2} d\tau \quad [A-1]$$

The integral is evaluated as $r_{0}^{2}3FC_{Al} \left( 1 + \frac{v_{d}d_{f}}{r_{0}} \right)^{3} - 1$. Also, by Faraday’s law $i_{p}$ in Eq. A-1 is replaced by $3FC_{Al}$. Rearrangement, Eq. 7 is obtained. The derivation of Eq. 8 proceeds from the general expression for $r_{-mean}$ in Eq. 6. According to the approximation, $dN_{p0}/dt$ in the integral can be replaced as in the preceding paragraph. Also, $N_{p0}$ is substituted with $i_{app}C_{V}r_{0}^{2}3FC_{Al}$ (Eq. 5). The result is

$$\frac{r_{2}}{r_{1}} = \frac{1}{r_{0}} \int_{0}^{\infty} \left[ 1 + \frac{v_{d}}{r_{0}} (t - \tau) \right]^{2} d\tau \quad [A-2]$$

Equation 8 results after the integral is evaluated as above.

List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$B$</td>
<td>field coefficient for high-field conduction, cm/V</td>
</tr>
<tr>
<td>$C_{Al}$</td>
<td>concentration of Al in metal, 0.1 mol/cm$^{3}$</td>
</tr>
<tr>
<td>$C_{v}$</td>
<td>interfacial capacitance, farad/cm$^{2}$</td>
</tr>
<tr>
<td>$C_{Al}$</td>
<td>concentration of Al$_2$O$_3$ in oxide film, 0.0304 mol/cm$^{3}$</td>
</tr>
<tr>
<td>$C_{v}$</td>
<td>concentration of voids in metal, cm$^{-3}$</td>
</tr>
<tr>
<td>$E$</td>
<td>electrode potential, V</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant, 96,487 C-equiv</td>
</tr>
<tr>
<td>$i_{app}$</td>
<td>pre-exponential current density for conduction, A/cm$^{2}$</td>
</tr>
<tr>
<td>$i_{p}$</td>
<td>current density for uniform corrosion, A/cm$^{2}$</td>
</tr>
<tr>
<td>$i_{p}$</td>
<td>current density for uniform corrosion, A/cm$^{2}$</td>
</tr>
<tr>
<td>$t_{app}$</td>
<td>applied current density, A/cm$^{2}$</td>
</tr>
<tr>
<td>$t_{rms}$</td>
<td>root-mean-square pit radius, cm</td>
</tr>
<tr>
<td>$r_{pit}$</td>
<td>radius of pit, cm</td>
</tr>
<tr>
<td>$r_{0}$</td>
<td>initial pit radius, cm</td>
</tr>
<tr>
<td>$t_{pit}$</td>
<td>time when pitting current supplies applied current, s</td>
</tr>
<tr>
<td>$v_{pit}$</td>
<td>dissolution velocity in pits, cm/s</td>
</tr>
<tr>
<td>$d$</td>
<td>oxide film thickness, cm</td>
</tr>
<tr>
<td>$e$</td>
<td>fraction of uniform oxidation-dissolution current contributing to oxide growth</td>
</tr>
<tr>
<td>$\phi$</td>
<td>potential drop through oxide film, V</td>
</tr>
</tbody>
</table>

References


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