A Mathematical Model for the Initiation of Aluminum Etch Tunnels

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Abstract
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Keywords
aluminum, corrosion, etching, passivation, dissolving, electrochemistry, mass transfer, modelling

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A Mathematical Model for the Initiation of Aluminum Etch Tunnels

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ABSTRACT

A mathematical simulation is presented which predicts the spontaneous shape evolution of cubic etch pits on aluminum as they develop into etch tunnels during anodic etching in chloride solutions. The simulation is based on a model for oxide passivation, according to which the rate of oxide film coverage increases as the potential at the dissolving surface is made more negative than the critical repassivation potential, which depends on the local chloride ion concentration. Mass transport calculations are used to predict the electrolyte concentration and potential in the pit, which in turn determine the rate of oxide advance and hence the shape change of the pit. The model predicts the pit-tunnel transformation, as well as width expansion of tunnels near their mouths. The occurrence of these features is independent of the choice of the passivation rate constant, an adjustable parameter in the simulation. Tunnel width oscillations were found at relatively low values of the rate constant. In the model, the pit-tunnel transformation is produced by rapid pit sidewall passivation, which is due to the relatively slower increase of the pit electrolyte concentration relative to the ohmic drop, during the pit's initial growth. A fully quantitative comparison of the model and experiment is possible with independent experimental information on passivation kinetics.

Introduction

An aluminum etch tunnel is a type of corrosion pit found after anodic etching in chloride solutions at temperatures above about 60°C. Among other forms of localized corrosion, the morphology of tunnels is unique in that dissolution occurs exclusively on the end or tip surface of the tunnel. As a result, tunnels penetrate into the metal rapidly, at velocities of several micrometers per second, while their widths change much more slowly. Tunnels are about 1 μm wide and can grow to lengths of 100 μm; their number density can approach 10⁷/cm². Tunnel etching is used in the fabrication of aluminum electrodes for electrolytic capacitors, where it serves to enhance the electrode's surface area.

Characteristic features of tunnel morphology and growth have been discussed by Alwitt et al.1 Tunnel growth occurs only in the <100> crystallographic directions. The growth velocity is independent of tunnel length but increases with temperature according to an Arrhenius dependence (activation energy 15 kcal/mol).2 The dissolving end or tip face is a flat and smooth (100) plane, while the sidewalls have a rough, corrugated texture (Fig. 1). These wall ripples can be viewed as tunnel width oscillations, which have a characteristic amplitude and wavelength of roughly 0.1 μm; available information suggests that these ripple dimensions do not depend significantly on temperature. The widths of tunnels near their mouths expand with increasing length (Fig. 2), while those of long tunnels taper slowly. At small etching times (<1 s), only half-cubic crystallographic etch pits, having (100) faces, are found on the surface, while after a few seconds, both etch pits and tunnels are present. This suggests that tunnels originate from etch pits, which transform into tunnels as they grow. After nucleation of etch pits, there is a stage of rapid dissolution in which they grow to sizes of 0.1–1 μm in a few milliseconds; afterward, their dissolution rate (or dissolution current density) is apparently constant and approximately the same as in tunnels.3 The dissolution rate in etch pits is uniform along their walls (Fig. 3).

Aspects of the growth mechanism of tunnels can be inferred from their morphology. The passivity of tunnel sidewalls can be attributed to the presence of a surface oxide film. While the tunnel end surface dissolves, new oxide film is continuously formed on the sidewalls. The observation that the dissolving tip surfaces of tunnels are always flat and smooth suggests that this new oxide is formed only at the edge of the tip surface. In effect, the leading edge of the oxide film (oxide front) moves in the direction of tunnel growth, at a velocity (denoted here as v₁) which is the same as that of dissolution (v₀). In contrast to tunnels, the sidewalls of cubic pits are free of oxide film; the transformation of pits into tunnels is attributable to oxide passivation of the pit sidewalls. The characteristic width expansion of tunnels near their mouths suggests that this sidewall passivation does not occur instantaneously; rather, the oxide front moves down the sidewall with a finite velocity, while the exposed sidewall surface below the oxide front dissolves laterally (see Fig. 4a). Since the oxide front eventually reaches the dissolving pit bottom, v₁ must be greater than v₀ while the pit sidewalls are being passivated. However, after the oxide front arrives at the pit bottom, the two velocities are equal and remain equal during the further growth of the pit as a tunnel.

From this view, the shape evolution of etch pits and their transformation to tunnels can be quantitatively modeled; provided that the film and dissolution velocities can be predicted during pit growth and are found to display the time dependence indicated above. The goal of this work was to theoretically predict the shape of an etch pit as it evolves into a tunnel during anodic etching. Success of this effort depends on the ability to mathematically describe metal dissolution and passivation processes which are of fundamental importance to a wide spectrum of corrosion processes. A good model would also guide the selec-
tion of etching conditions to obtain desirable tunnel shapes. As is seen, the model was found to predict the transformation, and the results of model calculations yielded characteristic features of tunnels such as width oscillations and width expansion near the tunnel base.

Theoretical Model

Description of oxide passivation.—Modeling the shape evolution of etch pits and tunnels depends on the predic-
tion of the velocities of dissolution ($v_d$) and of the oxide front ($v_p$). Since scanning electron microscopy (SEM) morphological measurements have indicated that the dissolution velocity is the same in pit and tunnels, it is assumed here that $v_d$ is constant during the transformation. The critical element in the model is, then, the prediction of the film velocity, $v_p$. A model for the film velocity can be drawn from prior work in which passivation in tunnels was characterized both during steady tunnel growth at constant applied current and following current step reductions during etching, and in both cases correlated with the solution composition and potential at the tunnel tip surface. The results of these investigations can be summarized as follows: (i) During tunnel growth at constant current, the AlCl$_3$ electrolyte concentration at the tunnel tip increases with increasing tunnel length and the pH and potential there decrease. These trends are attributable to the increase of the ohmic and mass transport resistance of the tunnel with its length. However, transport calculations showed that for tunnels up to 14 μm in length at 70°C, the potential at the tip remains within 1 mV of repassivation potential of aluminum

$$E_n([\text{Cl}^-]) = -B \log \frac{[\text{Cl}^-]}{[\text{Cl}^-]_0} + E_n([\text{Cl}^-]_0)$$  \[1\]

where $[\text{Cl}^-]$ and $[\text{Cl}^-]_0$ are the chloride ion concentrations at the dissolving surface and in the bulk. Hence, the condition $v_p = v_d$ for tunnel growth is associated with a potential at the tip surface close to $E_n$. (ii) Following step reductions of the applied current during tunnel growth, the passive film covers a portion of the tip surface in a time

Fig. 3. Schematic depiction of the cross section of a half-cubic etch pit showing the location of the hemisphere used as the boundary in the simulation (dashed semicircle). The half-cubic shape represents the initial pit shape assumed in calculations. $v_d$ is the dissolution velocity. The thick line represents the oxide film.

Fig. 2. Scanning electron micrograph of oxide replica of the etched aluminum surface showing width expansion of tunnels during their initial growth. Etching was in 1 N HCl at 0.200 A/cm$^2$ for 5 s. Etchant temperature (a) 70 and (b) 90°C. (Used by permission of R. S. Alwitt, micrograph acquired by H. Uchi).

Fig. 4. Schematic depiction of three pit geometries for which different differential equations were applied to calculate the shape change of the pit. The thick line represents the oxide film. $v_p$ is the dissolution velocity and $v_d$ the velocity of the oxide front. (a) Gradually expanding width. (b) Gradually contracting width. (c) Discontinuously expanding width.
smaller than 1 ms. The time scale of this rapid passivation is much smaller than that required for mass transport to cause the concentration to change significantly. Thus, passivation after current step reductions is not associated with changes in the solution composition at the tip. On the other hand, potential transient measurements indicated that the tip potential was significantly more cathodic than \( E_D \) while passivation was taking place. It was inferred that film velocities larger than the dissolution velocity are associated with cathodic departures of the potential at the tip surface from \( E_D \).

On the basis of these results, \( v_p \) is taken to be a function of the difference between the potential at the dissolving surface and \( E_D \). While the "true" mathematical form of the kinetic expression for \( v_p \) is unknown, it can be reasonably assumed that if the range of variation of the potential during the pit-tunnel transformation is small enough, a linear approximation is adequate

\[
\frac{v_p}{v} = 1 - k_v \eta
\]

where the repassivation overpotential \( \eta \) is defined as \( E_D - E_D(\text{Cl}^-) \). For convenience, \( v_p \) in Eq. 2 is normalized using the constant \( v_p \). Equation 2 has the desired features that \( v_p \) is larger than \( v \) when \( E_D \) is more negative than \( E_D \), but the two velocities are equal when the potential is \( E_D \). \( k_v \) is a rate constant for passivation. According to Eq. 1 and 2, \( v_p \) depends on both the electrolyte concentration in the pit, \( C \), and the current density in the pit, \( I \). Equation 2 is obtained from theories such as those based on salt films, which propose that passivation in pits depends on features of the pit solution composition alone (e.g., pH, chloride ion concentration, mass transfer rate) and not on the potential. However, the experiments cited in the preceding paragraph clearly demonstrate that \( v_p \) cannot be a function of concentration alone. During steady state, if the solution composition is changing, \( v_p \) is constant, and yet during transient current step experiments, the solution composition remains unchanged during the time when \( v_p \) increases sharply. It should be mentioned that studies of much longer etch tunnels suggest that the solution at the tunnel tip can be nearly saturated with \( \text{AlCl}_3 \), however, this is not the case in small etch pits and newly formed tunnels.

This model for passivation is phenomenological in character in that it is deduced from experimental observations and not constructed directly from a molecular-scale view of the process. It should be pointed out, however, that the model is consistent with expectations based on the presence on the dissolving surface of an adsorbed chloride ion layer, which shields surface metal atoms from passivating reactions. Therefore, the hemispherical approximation is consistent with other two-dimensional phases on electrodes, desorption would occur preferentially on the outer edge of the layer where the adsorbates have fewer neighbors and are hence more loosely bound than in the interior. According to the rate process determining \( v_p \) would be chloride desorption. It should be noted that when the cathodic potential shift is large, as in the current step experiments of Tak et al., desorption in the interior of the chloride layer would be possible, and this would lead to breakup of the adsorbed layer into patches, which they observed. In the present case of undisturbed tunnel growth, however, the departure of the potential from \( E_D \) is much smaller, and the adsorption model would suggest the confinement of passivation to the perimeter of the active tip surface.

**Mass transport model** — Knowledge of the electrolyte concentration in the pit is necessary to predict the oxide film velocity, \( v_p \), in Eq. 2 and hence the pit shape evolution. As a pit grows, the \( \text{H}^+ \) ions in the etchant are driven out of the pit by migration and are replaced by \( \text{Al}^{3+} \) ions dissolved from the metal. The metal ions undergo hydrolysis to produce more \( \text{H}^+ \), but it was estimated previously that hydrolysis does not become significant until the \( \text{Al}^{3+} \) concentration reaches about 1.3 M, larger than the concentrations under consideration here. Thus, the pit solution was approximated as an \( \text{AlCl}_3 \) binary electrolyte, whether the bulk etchant was \( \text{HCl} \) or \( \text{AlCl}_3 \). The simplification resulting from this approximation is considerable, since the concentration field in the pit is described by the single diffusion equation for \( C \), the concentration of the \( \text{AlCl}_3 \) binary salt.

\[
\frac{\partial C}{\partial t} = D \nabla^2 C
\]

The error introduced by the binary electrolyte approximation should be to overestimate the rate of chloride ion concentration, since diffusivity of \( \text{HCl} \) at 25°C is about two times larger than that of \( \text{AlCl}_3 \). There was no error when the etchant was \( \text{AlCl}_3 \) solution.

During the pit-tunnel transformation, the pit geometry is complex and changes with time as the oxide film advances down the pit sidewalls and the pit simultaneously grows. A three-dimensional transient model would be necessary to accurately describe the concentration field. However, a simulation based on such a complex model was not attempted. Instead, an approximate pit geometry was chosen which simplified calculations yet still allowed evaluation of the effect of pit growth and passivation on the evolution of the pit electrolyte concentration. In this approximation, the hemisphere is on an insulating plane (Fig. 3). The same geometric approximation was made by Vetter and Streibholz, and by Beck and Alkire, in their analyses of mass transport during early pit growth. The hemisphere radius is one-half the width of the pit opening and does not change with time, since the metal at the pit mouth is passive. The effect of pit growth and passivation on the concentration was modeled through a time-dependent current boundary condition on the hemisphere surface (see below). Therefore, the hemisphere approximation reduces the three-dimensional, transient pit geometry to a static, one-dimensional geometry. The diffusion equation in the region outside the hemisphere accounts for radial diffusion toward the bulk solution

\[
\frac{\partial C}{\partial t} = D \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right)
\]

Beck and Alkire suggested that the hemisphere approximation, since it neglects the mass-transport resistance inside the pit, underestimates the concentration increase in the pit by a factor of 3. This effect would be further offset by that due to neglect of \( \text{H}^+ \) ions in the pit. In any case, the rate of passivation is determined by \( \eta \), which depends on the potential and concentration in the pit. While the hemisphere potential and concentration are smaller than those inside the pit, they should have similar functional dependencies on time. Thus, it was possible to compensate for the effect of the hemisphere approximation through the choice of a larger value for the empirical passivation rate constant \( k_v \).
During etching, it is found that the slope of the pitting potential is 0.0337 V vs. a reference electrode with a liquid junction, such as Ag/AgCl, for a reversible to the chloride ion, such as ER(Cb). For a reference electrode located at the dissolving surface and pit mouth, ER was the state polarization curve. Its dependence on the concentration of various concentrations at 70°C. ER was the concentration field in A1C1, ER(Cb).

The repassivation overpotential was measured experimentally using aluminum polarization curves in A1C1, ER(Cb). The repassivation potential was measured experimentally using aluminum polarization curves in A1C1, ER(Cb). The solution of Eq. 4 together with the boundary conditions 5 and 6 and the initial condition 8 yields the pit concentration field was obtained in integral form for an arbitrarily varying it using Duhamel's theorem. This integral is based on the solution for a constant current density with time, which is available in analytical form. The result for C(t), the concentration at the hemisphere area is

\[ C(r, t = 0) = C_b + \frac{i_t^2}{2Jd^2} \int \left( \frac{i(t) - \frac{i_t}{2}}{a^2} \right) \exp \left( \frac{D(t - \gamma)}{a^2} \right) \, dt \]

Further details concerning Eq. 9 are given by Zhou. The repassivation overpotential—The driving force for passivation is the repassivation potential \( \eta_p \), or \( \eta_p = E_p(C_b) \). The repassivation potential was measured experimentally using aluminum polarization curves in A1C1, solutions of various concentrations at 70°C. ER was the zero-current intercept of the pitting branch of the steady-state polarization curve. Its dependence on the concentration was found to be represented accurately, for \( C < 4.0 \times 10^{-4} \), by the logarithmic relationship in Eq. 1. The slope \( B \) in Eq. 1 was found to be 0.0337 V vs. a reference electrode reversible to the chloride ion, such as Ag/AgCl. For a reference electrode with a liquid junction, such as a saturated calomel electrode (SCE), this would correspond to a slope of 0.0337 V + RT/F, or 0.107 V at 70°C.

The repassivation overpotential is given by

\[ \eta_p = E_p - E_p(C_b) = E_p - E_p(C_b) + 0.0337 \log \frac{C}{C_b} \]  

where the reference electrodes were taken to be Ag/AgCl electrodes, as were used for the measurement of \( E_p \). The liquid junction potential in Eq. 11 was calculated according to the methods given by Newman. The repassivation overpotential was found to be

\[ \eta_p = \frac{A(t) + \int_{r_0}^{r} \frac{dr}{\tau} + \frac{4RT}{3F} \int_{r_0}^{r} \left( \frac{d \ln (C(t))}{r} \right) + 0.0337 \log \frac{C}{C_b} }{16} \]

The first term on the right side of this equation is the negative of the ohmic overpotential in the pit, \( \eta_h \), and is proportional to the pit current. The second and third terms depend on the concentration profile of the pit and are referred to as the negative concentration overpotential, \( \eta_C \). Equation 12, since it includes activity coefficients and experimentally measured transport properties, accounts for nonideal transport and thermodynamic behavior, which were expected in the relatively concentrated solutions found in pits.

_Pit shape evolution._—When the repassivation overpotential was known, the film velocity \( v_f \) could be calculated from Eq. 2. This velocity, together with \( v_f \), determines the shape change of the pit, according to the equations given in this section. The shape of the pit was described in terms of four functions of time: \( r_1(t) \) and \( x_1(t) \), the coordinates of the bottom corner of the pit; and \( r_2(t) \) and \( x_2(t) \), the coordinates of the front edge of the oxide film. \( x_1 \) and \( x_2 \) are depths measured from the pit mouth, and \( r_1 \) and \( r_2 \) are radii (half-widths) measured from the center axis of the pit. The dependences of these variables on time are governed by three sets of geometric equations, which apply to situations where the tunnel width near the dissolving surface is either expanding gradually, contracting gradually, or expanding discontinuously. These possible shapes (as depicted in Fig. 4) include all possible situations during pit growth.

_Gradually expanding width._—These equations apply when \( x_1 > x_2 \) and \( r_1 = r_2 \) and \( \eta_p < 0 \). This situation is typically found when, as shown in Fig. 4a, the oxide front is located on the pit sidewall during early pit growth. The equations are

\[ \frac{dr_1}{dt} = \frac{dr_2}{dt} = \frac{dx_2}{dt} = v_f \]

The last of these equations was derived from the geometric formula for the length of a curve. Once these functions are known by integration, the active surface area is calculated according to

\[ A(t) = 4 \pi r_1^2 + 8 \pi r_2(x_2 - x_1) \]

_Gradually contracting width (Fig. 4b)._—These equations are followed when \( x_1 > x_2 \) and \( r_1 > r_2 \) and \( \eta_p < 0 \). This situation occurs during the width oscillations which take place after tunnel growth is established. The equations are

\[ \frac{dr_1}{dt} = \frac{dr_2}{dt} = \frac{dx_2}{dt} = v_f \]

the active area is

\[ A(t) = 4 \pi r_1^2 \]
Discontinuously expanding width (Fig. 4c).—A discontinuity in the width occurs at any time if \( \eta_s > 0 \). The dissolution velocity then momentarily exceeds the passivation velocity, causing the pit width to increase with time at the location of the oxide front. It is seen below that width discontinuities occur momentarily during the tunnel width oscillations. The equations are

\[
\begin{align*}
\frac{dr_5}{dt} &= \frac{dr_{0s}}{dt} = v_y \\
\frac{dr_1}{dt} &= \frac{dr_{0s}}{dt} = v_z \\
\end{align*}
\]

In these equations, the upward dissolution of the top active surface was neglected for simplicity. The active area is

\[
A(t) = 4r_5^2 + 8r_3(x_2 - x_1) + 4(r_5^2 - r_1^2)
\]

Calculations.—The equations of the model are the geometric pit shape equations, Eq. 13–18, along with Eq. 2, 9, and 12. The dependent variable are \( C, \eta, \eta_s, \eta_o, \eta_t, \eta_i, r, t, A, r_3, x_2, r_1, x_1 \). The simulation was carried out using the fourth-order Runge–Kutta algorithm to solve the pit shape equations. The time step for integration was taken as \( 1 \times 10^{-4} \) s, which was small enough to obtain convergence of the dependent variables. The integrals in Eq. 9 were calculated by Simpson’s rule. Further details of the numerical calculation procedure are given by Zhou.19

The simulations required knowledge of transport properties and activity coefficients as functions of concentration at the etching temperature (70°C). Activity coefficients were predicted from Meissner’s correlation for aqueous electrolyte solutions20 and were known up to a concentration of 4.0 N. The conductivity was previously measured by Hebber.21 The diffusivity was found from potential transients accompanying constant diffusion. Diffusion during tunnel etching was determined to be approximately constant at \( 2.1 \times 10^{-5} \) cm/s for concentrations at the dissolving surface up to about 4.0 N. The Al³⁺ ion transfer number was determined with concentration cell potential measurements.22 For these experiments, one compartment of the cell contained 1.0 N AlCl₃ and the other an AlCl₃ solution of variable concentration. The potential between Ag/AgCl electrodes in each compartment was measured. The cation transfer number \( i^5 \) was found to be approximately constant at 0.21 up to concentrations of 4 N.

Results and Discussion

Repassivation overpotential during steady-state diffusion.—Before presenting the simulation results, two calculations are described which facilitate their interpretation: a calculation of \( \eta_s \) for steady-state diffusion in pits and tunnels, and a comparison of the electrolyte concentration in the pit to that expected if diffusion were at steady state. A similar calculation to the first one was given by Hebert and Alkire,4 but it did not fully incorporate experimental values for the thermodynamic and transport parameters. It is shown in the Appendix that steady-state diffusion is a good approximation during the growth of developed tunnels. At steady state, only aluminum ions carry current in the binary electrolyte, and hence the current density in solution is \( 3FN\eta_{Al} \). The following relation then holds between the current density \( i \), at a given point in the solution and the local concentration gradient

\[
\frac{iL^2}{3FD} = -\frac{\partial C}{\partial r}
\]

Using this relationship, the ohmic overpotential in Eq. 12 can be transformed into an integral over concentration. The resulting expression for \( \eta_s \) is

\[
\eta_s = -3F \int\left[ \frac{D}{i\eta^5} dC + \frac{4RT}{3F} \int \frac{J(t)}{C_0} dln(C_f + J) + 0.0037 \log \frac{C_0}{C_f} \right]
\]

At steady state, \( \eta_s \) depends only on \( C \), and does not depend directly on the pit geometry (it depends indirectly on geometry through \( C_f \)). In fact, Eq. 20 may be applied to pits as well as to tunnels of any length. In the latter case, \( C_f \) refers to the concentration at the tunnel tip. In contrast to pits, diffusion in tunnels is more nearly at steady state, because the dissolution current, which is proportional to the tip area, is approximately constant with time.

The calculated steady-state \( \eta_s \) values for a bulk solution of 1 N AlCl₃ at 70°C are shown in Fig. 5, which also displays the concentration overpotential \( \eta_c \) and ohmic overpotential \( \eta_R \). The calculation was stopped at a concentration of 4 N (1.33 M), beyond which activity coefficients were unavailable. A tunnel of length about 14 µm would have this concentration at its dissolving tip surface. Figure 5 shows that the magnitudes of both overpotentials, which are opposite in sign, are significant, increasing monotonically with surface concentration to 42 mV. However, strikingly, \( \eta_c \) and \( \eta_s \) nearly cancel in the calculation of \( \eta_R \), the average and maximum \( \eta_s \) are 0.46 and 0.86 mV, respectively. The refinement of Hebert and Alkire’s calculation thus brings \( \eta_s \) much closer to zero than was the case in their paper and supports the hypothesis that during tunnel growth, the potential at the tunnel end is close to the repassivation potential. Also, since Eq. 20 does not depend on geometry, steady-state diffusion in pits would also imply equality of \( \eta_c \) and \( \eta_s \). However, this suggests that the pit-tunnel transformation would not occur, since the oxide front would never overtake the pit bottom. Therefore, a calculation is given in the next section which demonstrates that diffusion in pits, in contrast to tunnels, is not at steady state.

Transient diffusion during pit growth.—The purpose of this calculation is to demonstrate the effect of transient diffusion during pit growth on the pit electrolyte concentration. Unlike the mass transfer model in the simulation, the pit sidewalls were taken to be uniformly dissolving and free of oxide. The pit geometry is approximated by a hemisphere, as in Fig. 3. However, since the sidewalls were dissolving, the hemisphere radius increases with time at a rate given by the dissolution velocity \( v_y \). The calculation thus includes transient diffusion effects associated with both the increasing pit current and its increasing size. The diffusion equation is

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial r^2}
\]
\[
\frac{\partial C}{\partial t} - v_0 \frac{\partial C}{\partial y} = D \frac{\partial}{\partial y} \left( y \frac{\partial C}{\partial y} \right)
\]

where the second term on the left side represents the convective flow of electrolyte into the pit. The boundary condition Eq. 5 is imposed at infinite radius and zero time, and Eq. 6 holds at the surface of the growing hemisphere, \( r = r_f \). The radial coordinate is first transformed to the reference frame of the hemisphere, according to \( y = r - r_f \), which results in

\[
\frac{\partial C}{\partial t} - 2v_0 \frac{\partial C}{\partial y} = D \frac{\partial^2 C}{\partial y^2} + \frac{2}{y + v_f t} \frac{\partial C}{\partial y}
\]

In terms of the new variable \( y \), the boundary condition Eq. 6 is imposed at \( y = 0 \), while Eq. 5 holds at infinite \( y \) and zero time. Equation 22 was solved numerically using the method of lines (IMSL subroutine MOLCH). Figure 6 shows the concentration at the hemisphere surface, \( C(y = \infty, t) \), as a function of the hemisphere radius or pit depth, \( v_f t \). Results for three different constant dissolution current densities are given (solid curves), and for each \( i_C \) the prediction is compared to that based on steady-state diffusion at the current pit depth, from Eq. 8 (dashed curves). The current densities range from the tunnel current density at \( 0.5 \mu \text{A/cm}^2 \) to the typical current density for the rapid initial growth of small pits under these conditions, \( 150 \mu \text{A/cm}^2 \). Despite the brief duration of this rapid initial dissolution (about 10 ms, corresponding to a pit depth of \( 0.5 \mu \text{m} \)), the calculations were carried through to a depth of \( 3 \mu \text{m} \). Saturation of \( \text{AlCl}_3 \) is reached at a concentration of approximately \( 3 \text{ M} \). The convective term in Eq. 22 was found to be small and does not influence the prediction.

Figure 6 shows that the pit concentration is always smaller than the concentration expected if diffusion were at steady state. The departure from steady state increases as the dissolution rate becomes larger. Thus, the effect of transient diffusion is to decrease the magnitude of the concentration overpotential in Eq. 12 relative to steady-state diffusion; by comparison, the ohmic overpotential is much less sensitive to concentration. During pit growth, the concentration and ohmic overpotentials would not cancel as in Fig. 5, and a negative repassivation overpotential \( \eta_{\text{R}} \) should be expected. As a result, according to Eq. 2, \( v_f \) should be larger than \( v_0 \), and the oxide front would eventually overtake the pit bottom, as required for the pit-tunnel transformation. Thus, rapid sidewall passivation should be expected to occur in the simulation, which includes transient diffusion due to the increase of the pit active area with time. This passivation may be attributed to a repassivation overpotential generated by the pit's own rapid dissolution.

Prediction of tunnel initiation at the reference etch conditions. — The results of model calculations for the reference etch conditions are presented in this section. These conditions are the following: temperature \( 70°C \); bulk etchant concentration \( 1 \text{ N AlCl}_3 \); initial pit radius \( 1.2 \mu \text{m} \); passivation rate constant \( 8000 \text{ V}^{-1} \). The rate constant \( (k_r) \) was chosen arbitrarily since it is an unknown parameter; the effect of \( k_r \) on the simulation results is discussed in the following section. The dissolution velocity \( v_f \) was taken to be \( 2.1 \mu \text{m/s} \) from experimental measurements of tunnel growth rates at \( 70°C \).

According to the pit shape profile (Fig. 7), the pit width initially expands linearly with increasing depth, and then, after \( 0.50 \text{ s} \), decreases rapidly to an approximately constant value of \( 4.2 \mu \text{m} \) which is maintained indefinitely as dissolution continued. In this "constant" width region, the width oscillates about its average, with a wavelength and amplitude of \( 0.1 \) and \( 0.06 \mu \text{m} \), respectively. It is clear that the initial pit, whose side and bottom faces were uniformly dissolving, has spontaneously transformed into a tunnel with passive sidewalls and dissolution only on the bottom face. Tunnel formation is insensitive to the choice of input parameters used for the calculations. The simulated tunnel exhibits width expansion near the base, as well as wall ripples during tunnel growth, both of which, as discussed in the Introduction, are characteristic features of etch tunnels. The overshoot of the tunnel width above its steady-state value, which was frequently found in simulations, was not clearly detectable in SEM micrographs. However, the width overshoot is usually a fairly small fraction of the mean tunnel width (0.062 in Fig. 7) and it was not present.
at large $k_v$ values. In the following paragraphs, events during the simulation are described in detail.

At early times during the simulation, the sidewalls are relatively free of oxide and the active area increases rapidly. The resulting transient diffusion generates a negative repassivation overpotential, and $v_o$ is about 2.5 times larger than $v_p$ (Fig. 8). However, as the oxide front approaches the pit bottom, the lateral expansion of the pit occurs more slowly, since the sidewalls are nearly covered with oxide. Consequently, the active area becomes nearly constant with time (Fig. 9), the concentration begins to approach repassivation overpotential, and $v_o$ is about 2.5 times larger. The resulting transient diffusion generates a negative relatively free of oxide and the active area increases rapidly which slightly positive can be attributed to the model’s discontinuity at $v_R = 0$. In fact, however, tunnel width is not constant, but instead it oscillates about a mean value. These oscillations can be attributed to the model’s discontinuity at $v_R = 0$, in which slightly positive $v_R$ values cause the tunnel width to increase without bound (Fig. 4c). Such small positive values of $v_R$ were found to occur in the course of numerical calculations during the time step after which $v_p$ approaches zero to within $-10^{-7}$ V. The origin of the discontinuity is that when $v_R$ is even slightly positive, $v_p$ becomes smaller than $v_p$ and consequently, the film lags behind the pit wall as it dissolves laterally outward. The expansion of the active area causes the current from the pit to increase with time, and a sequence of events initiates similar to those during the initial period of increasing current: the width first increases until the oxide front reaches the bottom face of the tunnel and then it contracts until $v_p$ equals $v_p$. This cycle of events then repeats itself after $v_R$ again momentarily becomes positive.

The width oscillations in the simulation simulate a possible physical mechanism for tunnel wall ripples. The small positive excursions of $v_R$ during numerical calculations, which initiate wall oscillations, model small natural disturbances in the potential during tunnel growth. Because the magnitude of a potential disturbance needed to initiate a ripple is very small (less than 0.1 mV), these disturbances could be associated with random events which occur outside the tunnel itself. Examples of such events might be hydrogen bubbles breaking off the external surface or passivation of other pits or tunnels. The tunnel would be only susceptible to these disturbances at the point in the cycle when the width is at a minimum and $v_R$ is close to zero; at other times $v_R$ is too large to be affected by small fluctuations. Thus, for a frequency of disturbances larger than the predicted frequency of ripples (about 2 Hz), a ripple profile like that in Fig. 7 should be expected. This is likely, since the rates of pit nucleation and passivation, which would be sources of potential disturbances, are usually greater than $10^{-5}$ cm$^2$/s. 

Effect of passivation rate constant $k_v$ on the evolution of pit geometry.—Since the value of the passivation rate constant $k_v$ has at this point not been experimentally determined, calculations were carried out to demonstrate the effect of its variation on the tunnel shape. In these calculations, all input parameters except $k_v$ were set at the reference etch conditions given in the previous section. $k_v$ was varied from $1 \times 10^4$ to $4 \times 10^4$ V$^3$.

The expansion slope (initial value of $dr/dz$) is shown in Fig. 10, along with the average $v_p$ prior to the constant width, normalized by the dissolution velocity $v_p$. As expected, increasing $k_v$ causes the film velocity to increase, and this reduces the expansion slope. There is an apparent saturation of $v_p$ and the expansion slope beyond $k_v$ of about $1.5 \times 10^4$ V$^{-1}$; increasing $k_v$ above this value does not significantly change the tunnel shape. In this limiting shape, as the oxide front moves into the pit, the active area is constant with time. If the area $A(t)$ is constant at the initial value of $12$ cm$^2$, then Eq. 14 can be solved for $x(t)$ during the initial expansion of the pit.

$$\frac{x}{a} = \frac{3}{4} \left( \frac{v_p}{a} \right) - \frac{3}{2} \left( \frac{v_p}{a} \right) - \frac{1}{2} \left( \frac{v_p}{a} \right)$$  

[23]
During this same period, \( r/a = 1 + (v_{\text{f}}/a) \). By dividing the slope of this equation by that of Eq. 23, the average expansion slope, \( dr/dx_1 \), of 0.41 is obtained at times less than 0.5 s. This is the limiting behavior approached in Fig. 10 for large \( k_c \). When \( k_c \) is very large, only an extremely small transient increase of active area during pit growth is sufficient to drive rapid motion of the oxide front into the pit; consequently, the active area remains nearly at its initial value as the pit grows. The corresponding limiting value of \( v_p \) in Fig. 10 was obtained by solving Eq. 13 after insertion of \( dx_1/dt \) from Eq. 23.

According to Fig. 11, the average tunnel width (normalized by dividing by the initial pit width \( 2a \)) follows the same trend with \( k_c \) as the expansion slope. Thus, the final tunnel width is determined primarily by the rate of width expansion from the base. Figure 11 also shows the overshoot fraction, defined as the overshoot in width divided by the average tunnel width. The overshoot fraction approaches zero in the constant-area limit for large \( k_c \) but increases rapidly when \( k_c \) is reduced to small values. The width overshoot is determined by the magnitude of the repassivation overpotential during the initial width expansion, since the width contraction continues until \( \eta_\alpha \) becomes zero. The total contraction is large at small \( k_c \), because \( \eta_\alpha \) is large during the width expansion and must be reduced by a large amount during the contraction. In the limit of large \( k_c \), on the other hand, the active area is nearly constant with time, and the extent of the contraction approached zero. The lack of width overshoot suggested by SEM micrographs implies that the actual \( k_p \) may be close to this limiting behavior.

The amplitude and wavelength of wall ripples are shown in Fig. 12 as functions of \( k_p \). The amplitude decreases with \( k_p \) and approaches zero in the constant-area limit. The behavior of the concentration and potential during the expanding-width portion of a ripple is similar to the initial width expansion of the pit, and the contracting-width portion of the ripple is similar to the contraction of the pit area after the point of maximum width. Thus, the amplitude decreases with \( k_p \) for the same reasons as those given for the decrease of both the expansion slope and the overshoot fraction with \( k_c \). Also, as \( k_c \) is reduced, the oxide front moves slowly during both width expansions and contractions, causing the wavelength of ripples to increase.

Comparison with experimental tunnel shapes.—As discussed previously, the model predictions yield important qualitative characteristic features of the tunnel shape, such as approximately constant width, width expansion near the base, and sidewall ripples. Quantitative comparison of the predicted tunnel shapes with experiment is tentative, since experiments to measure the rate constant \( k_c \) have not yet been carried out. However, some similarities and differences between the model predictions and the SEM micrographs in Fig. 1 and 2 can be pointed out. From the figures, approximate wavelengths and amplitudes of wall ripples are 0.1 and 0.03 \( \mu \)m, respectively, and there is no detectable width overshoot. The ripple dimensions are predicted when \( k_p \) is around \( 1 \times 10^4 \text{ V}^{-1} \); however, the width overshoot at this \( k_p \) is about 5%, and it does not become negligible (less than 1%) until \( k_p \) is increased to about \( 2.5 \times 10^4 \text{ V}^{-1} \), at
which the ripple dimensions in the simulation are much smaller than those found in micrographs. This may suggest that the true \( k \) is at least \( 2.5 \times 10^4 \ \text{V}^{-1} \), and some other mechanism produces the observed wall ripples.

Another discrepancy is that the rate of passivation in the model calculations may be somewhat smaller than that suggested by etching morphologies. This slow passivation is manifested by the expansion slopes of the tunnels in Fig. 2, which are smaller than those predicted by the model. The expansion slope is 0.45 when \( k \) is 1 \( \times 10^4 \ \text{V}^{-1} \); the expansion slopes of the tunnels in Fig. 2 are at most 0.3–0.4, and some of the tunnels have significantly smaller slopes. As discussed previously, passivation in the simulations may occur more rapidly, the rate given by a constant active area \( A(t) \), and this maximum rate produces a minimum expansion slope of 0.41.

A possible explanation for the occurrence of rapid passivation in pits is suggested by the concentration transients during rapid initial pit growth (Fig. 6). The simulation assumes that no passivation occurred during the rapid initial growth of pits, during which the dissolution current density is roughly 100 A/cm\(^2\). It was thought that \( v_0 \) was likely to be much larger than \( v_0 \) during this time. However, Fig. 6 shows that when the dissolution current density is 150 A/cm\(^2\), the difference between the transient and steady-state concentrations is large, even when the pit depth is smaller than 1 \( \mu \text{m} \). As a result, the repassivation overpotential and \( v_0 \) would, in fact, be large. Moreover, when the growth rate is large, both the increasing pit current and its increasing size (the "moving boundary" effect) should contribute to the deviation of the concentration from steady-state diffusion; only the effect of increasing current was included in the simple mass-transfer model of the simulation. Hence, the oxide front would have moved faster than the velocity required to preserve a constant active area, and the expansion slope would have been smaller than the minimum of 0.41 in the simulation. If the effect of the moving boundary were included in the simulation and passivation were allowed to occur during early pit growth, it is likely that the predicted expansion slope would have been closer to those observed.

A final apparent discrepancy is that in the SEM micrograph in Fig. 2, the mean tunnel width continues to increase at the tunnel grows, while the model predicts it to be constant after a depth of 2 \( \mu \text{m} \). Again, the continued width expansion may result from a transient diffusion effect owing to the increase of the tunnel length with time. Since such moving boundary effects are not included in the present simulation, it was impossible to predict this feature of the tunnel morphology. It should be noted that with other surface pretreatments, parallel-sided tunnels are found under the same etching conditions.

**Conclusions**

A mathematical simulation was developed which predicts the spontaneous shape evolution of etch pits on aluminum as they develop into etch tunnels during anodic etching in chloride solutions. The model is based on two major concepts: (i) passivation takes the form of the movement of the leading edge of the oxide film into the pit along its side-walls; and (ii) the oxide front velocity is a function of the difference between the potential at the dissolving surface and the critical repassivation potential, whose value depends on the local chloride ion concentration. These concepts are derived from prior experiments and observations about the development of tunnel morphology. The simulation predicts the spontaneous pit-tunnel transformation and the width expansion of tunnels near their bases, as well as the presence of tunnel width oscillations. It was found that the repassivation overpotential (difference between the potential and repassivation potential) needed to passivate the pit sidewalls during the transformation is generated by transient diffusion during pit growth, since the potential drop in the pit increases rapidly relative to the pit concentration overpotential. When the oxide front reaches the bottom surface of the pit, the rate of oxide advance slows and then oscillates around the metal dissolution rate as the pit continues to grow as an etch tunnel. The pit-tunnel transformation is fond to occur independently for the assumed value of the passivation rate constant, an unknown parameter. Quantitative comparison of the model and experiment was limited by the present lack of independent information on this rate constant. However, the passivation rates predicted by the model are somewhat smaller than those implied by the geometries of actual pits. This discrepancy is thought to arise because the simulation does not allow passivation during the rapid initial growth of pits and does not include the effect of the moving boundary associated with the dissolving surface.

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**APPENDIX**

This appendix examines the steady-state approximation for diffusion during tunnel growth and also the importance of convection in the tunnel. The diffusion equation for the AlCl\(_3\) binary electrolyte in the tunnel is

\[
\frac{\partial C}{\partial t} + v_0 \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial z^2} \tag{A-1}
\]

In this equation, the tunnel geometry is represented as parallel-walled. Hebert and Alkire showed that even when the walls are tapered, it is possible to transform the tunnel to this geometry.\(^6\) The boundary conditions are

\[
C(z = 0) = C_0 \tag{A-2}
\]

\[
\frac{\partial C}{\partial z}(z = v_0 t) = 0 \tag{A-3}
\]

The boundary at \( z = v_0 t \) moves as the tunnel grows. The problem is transformed to one with stationary boundaries using the transformation \( x = z/(v_0 t) \). In addition, the following dimensionless variables are defined

\[
\theta = \frac{C}{C_0}, \quad \tau = \frac{t v_0}{3FDC_0} \tag{A-4}
\]

The differential equation then becomes

\[
\tau \frac{\partial \theta}{\partial \tau} = -(1 - z^2) \frac{\partial \theta}{\partial z} + \frac{N}{\tau} \frac{\partial^2 \theta}{\partial z^2} \quad (z = 0) \tag{A-5}
\]

For a tunnel growth time of 10 s, using parameter values used elsewhere in the paper, \( \tau = 5.0, N \) has a value of 240, and \( x \) is between zero and one. Hence it is seen that the second derivative term on the right side of Eq. A-4 is about 50 times larger than the other terms. This indicates that neither convection nor transient-diffusion effects should be significant during undisturbed growth of developed tunnels. Diffusion in tunnels is at steady state to a good approximation.
**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>A</td>
<td>actively dissolving area in pit, cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>a</td>
<td>one-half width of pit opening, cm</td>
</tr>
<tr>
<td>B</td>
<td>empirical constant relating ( E_p ) to ( \log [\text{Cl}^-] ), V</td>
</tr>
<tr>
<td>C</td>
<td>electrolyte concentration, mol/cm&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>C&lt;sub&gt;b&lt;/sub&gt;</td>
<td>bulk solution electrolyte concentration, mol/cm&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>C&lt;sub&gt;s&lt;/sub&gt;</td>
<td>electrolyte concentration at dissolving surface pit or tunnel, mol/cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>D</td>
<td>electrolyte diffusion coefficient, cm&lt;sup&gt;2&lt;/sup&gt;/s</td>
</tr>
<tr>
<td>E&lt;sub&gt;r&lt;/sub&gt;</td>
<td>repassivation potential, V</td>
</tr>
<tr>
<td>F</td>
<td>electrode potential at dissolving surface of pit or tunnel, V</td>
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<td>( F )</td>
<td>Faraday constant, 96487 C/equiv</td>
</tr>
<tr>
<td>( f )</td>
<td>mean molar electrolyte activity coefficient</td>
</tr>
<tr>
<td>( i )</td>
<td>current density, A/cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>( i_0 )</td>
<td>metal dissolution current density, A/cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>( k_t )</td>
<td>rate constant of surface film coverage, V&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>M</td>
<td>molecular weight of metal, g/mol</td>
</tr>
<tr>
<td>( N_{\text{Al}^3} )</td>
<td>molar flux of Al&lt;sup&gt;3+&lt;/sup&gt; ions in solution, mol/cm&lt;sup&gt;2&lt;/sup&gt;s</td>
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<tr>
<td>( R )</td>
<td>gas constant, 8.314 J/mol K</td>
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<tr>
<td>( r )</td>
<td>radial coordinate, cm</td>
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<tr>
<td>( r_1, r_2 )</td>
<td>width-direction coordinates of oxide front and bottom corner of pit, cm</td>
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<tr>
<td>( T )</td>
<td>absolute temperature, K</td>
</tr>
<tr>
<td>( t )</td>
<td>time, s</td>
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<tr>
<td>( t_1', t_2' )</td>
<td>Al&lt;sup&gt;3+&lt;/sup&gt; and Cl&lt;sup&gt;-&lt;/sup&gt; transference numbers, dimensionless</td>
</tr>
<tr>
<td>( v_0 )</td>
<td>metal dissolution velocity, cm/s</td>
</tr>
<tr>
<td>( v_p )</td>
<td>velocity of oxide film coverage (rate of oxide front advance), cm/s</td>
</tr>
<tr>
<td>( x_1, x_2 )</td>
<td>length-direction coordinates of oxide front and bottom corner of pit, cm</td>
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</table>

**Greek**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>( \gamma_n )</td>
<td>concentration overpotential inside pit or tunnel, V</td>
</tr>
<tr>
<td>( \gamma_{n_0} )</td>
<td>ohmic overpotential at dissolving surface relative to repassivation potential, V</td>
</tr>
<tr>
<td>( \rho )</td>
<td>density of metal, g/cm&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>( \rho_{\text{Cl}^-}, \rho_{\text{Cl}^+} )</td>
<td>electrochemical potentials of Cl&lt;sup&gt;-&lt;/sup&gt; ions in bulk and at dissolving surface, J/mol</td>
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**REFERENCES**