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Abstract
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Keywords
aluminum, pattern formation, etching, surface chemistry, passivation, scanning electron microscopy, dissolving

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Comments
Passivation of Surfaces within Aluminum Etch Tunnels

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ABSTRACT

Transient events accompanying passivation of active surfaces in aluminum etch tunnels are investigated. Passivation is induced by pulsed reductions of the anodic etching current, of several milliseconds duration. Scanning electron microscopy is used to measure the area passivated. Potential transients are analyzed to identify a possible potential driving force for passivation. For the experimental conditions of this work, at 0.13 ms after the current step, there is a temporary reduction in the metal dissolution current in tunnels. The change in dissolution current is proportional to the cathodic surface overpotential, relative to the critical repassivation potential. The transient reduction in dissolution current is associated with passivation, since no variation in dissolution current with potential is observed during steady tunnel growth. Surface changes resulting in permanent passivation occur later, at times between 3 and 12 ms after the current step.

The growth of corrosion pits is arrested by coverage of the active pit surface with a passive oxide film. The passivation reaction thus determines the stability of pit growth; passivation of active surfaces in localized corrosion is also an important consideration in the propagation of stress corrosion cracks. Phenomenologically, pits stop growing when the electrode potential is brought below a critical repassivation potential. It was suggested that deviations of the potential at the metal surface from the repassivation potential control passivation. The present work is an investigation of the kinetics of development of passive surfaces within aluminum etch tunnels. If Hebert and Alkire’s suggested mechanism is correct, there would be a correlation between the rate of passivation and cathodic overpotential relative to the repassivation potential.

Rapid passivation is induced through pulsed reductions of the anodic applied current etching. Alwitt et al. (9) observed evidence of rapid passivation in tunnels after step decreases in the applied current during etching. The current steps caused abrupt constrictions in the widths of tunnels; part of the active tunnel tip area repassivated, while the remaining active surface continued to dissolve. Current pulses rather than steps are used in the present work to induce passivation. The current is stepped to a lower value during etching and held there for a time of several ms before being stepped back to the original current. The pulse time controls the amount of area passivated. After the experiment, the constrictions in tunnel width, caused by partial passivation of the tip surface, were measured using scanning electron microscopy. The transient progress of passivation is inferred through measurement of the area of the passivated surface, as a function of the pulse time. Potential transients are interpreted to identify the potential driving force for passivation.

Experimental

One lot of high-cubicity aluminum foil (99.99% purity, Toyo) was used in all experiments. The high-cubicity characteristic refers to a high proportion of surface grains having (100) faces exposed. Etch tunnels were the dominant corrosion structures. Solutions used for etching and pretreatment baths were prepared using reagent grade chemicals.

A glass holder for the Al foil was used in etching experiments, which allowed 5.07 cm² of Al surface to contact the...
etching solution. The counter-electrode was a Pt wire bent into a semicircle and fixed on the holder. The reference electrode (Ag/AgCl/4 M KCl, Fisher) was placed behind the glass holder during experiments; in this position, the measured value of the potential was insensitive to the exact location of the reference electrode. The etchant bath was agitated with a magnetic stirring bar during experiments. There was no preferential concentration of pits on any part of the electrode surface.

Two pretreatments were used for the Al foils: (i) 5 min immersion in 1 N HCl solution at room temperature, and (ii) 20 min immersion in 1 N NaOH solution at room temperature, followed by washing with water, and then a 1-2 h drying period before etching. The effect of the pretreatment on passivation in tunnels is discussed below. After pretreatment, the foils were mounted in the holder, and immersed in the etchant solution. The applied current was initiated immediately upon immersion. A potentiostat/galvanostat (PAR 273) was used to supply the applied current during etching. A personal computer (Zenith 158) and RS232C interface were employed to execute the etching experiments. Rapid potential transients were measured using a high-resolution digitizer (Keithley 194A). AC modulation of the applied current for current cycling experiments was carried out using a pulse generator (Datapulse 108A) whose output was sent to the potentiostat/galvanostat. When polarization was complete, the foils were removed immediately from the etchant bath and rinsed with water.

The morphology of etch tunnels was studied using a scanning electron microscope (JEOL-JSM 840). In order to observe the three-dimensional structures of tunnels, oxide replicas of the etched surfaces were formed (12). Oxide replicas were sputter coated with gold prior to electron microscopic examination. The weight loss from foils during etching was determined using an electronic balance (Mettler AE163).

Tunnel growth rates were determined using the superimposed ac technique (13). In 1 N HCl solution at 65°C, the growth velocity was 2.1 μm/s. The metal dissolution current density equivalent to this growth velocity is 6.1 A/cm². For the results in Fig. 2, a different lot of foil was used for which the tunnel growth rate was 1.8 μm/s under the same conditions. However, the shapes and surface distribution of tunnels were similar for the two lots of foil.

**Results and Discussion**

Tunnel morphology in current pulse experiments.—Figure 1 shows details of oxide replicas of the tunnel structures produced in two etching experiments in which 4 and 12 ms current pulses were superimposed on the etching current. To assist in the identification of constrictions in width produced by the pulses, three successive current pulses were applied at an interval of about 1 s. Figure 1 shows that the current steps induce a sudden reduction in the tunnel tip area, caused by passivation. The remaining unpassivated surface of the tunnel continues to corrode after the current step. After the constrictions, expansion of the tunnel width and shifting of its axis are sometimes observed. However, these events occur after the times of interest in the present work, and will not be considered here. It can be seen that the 12 ms pulse induced larger constrictions than did the 4 ms pulse. At constrictions, the relative positions of the passivated surface and the emergent tunnel were variable. When measuring the area of the flat passivated surface at a constriction, samples were rotated in the SEM to view all sides of the tunnel.

When the Al had been pretreated by a 5 min immersion in 1 N HCl solution at room temperature, no constrictions in tunnel width were observed after current step experiments. Apparently the current reduction caused some tunnels to completely passivate while others experienced no passivation. On the other hand, when the NaOH pretreatment was used, constrictions were observed, similar to those shown in Fig. 1, in both current step and current pulse experiments. The NaOH pretreatment was used for all experiments reported in the present work.

The effect of pretreatment on the appearance of constrictions may be related to the difference in tunnel length distributions between the two pretreatments. Figure 2 shows that the tunnels produced after the NaOH pretreatment in constant current experiments are all of relatively uniform length. On the other hand, a wide distribution of tunnel lengths was observed in constant current experiments using the Al foils pretreated by a 5 min immersion in 1 N HCl solution at room temperature.
lengths, similar to that reported by Beck et al. (14), is present when the HCl pretreatment is used before constant current experiments. The dependence of the length distribution on pretreatment may be caused by changes in the surface oxide film due to pretreatment, which influence pit nucleation.

Transport considerations can be used to explain the influence of the tunnel length distribution, as determined by the pretreatment, on uniformity of passivation. The tunnel transport model in Ref. (11) indicates that both the ohmic and concentration overpotentials relative to the repassivation potential increase with increasing tunnel length. The calculations in Ref. (11) further showed that during steady state current growth, the ohmic and concentration overpotentials nearly cancel, so that the tip surfaces of all tunnels, independent of their lengths, are maintained near the repassivation potential. However, after the step reduction in current, the ohmic overpotential in the tunnel is reduced abruptly, but the concentration overpotential adjusts to the lower current only after a period of transient diffusion. During this period, if there is a distribution of tunnel lengths (and a corresponding distribution of ohmic overpotentials), the tip surfaces of tunnels are at different potentials relative to the repassivation potential. Therefore, nonuniform passivation in this case is consistent with the concept of control of passivation by a critical potential.

The results of a number of current pulse experiments are shown in Fig. 3. In all experiments, the current was reduced to 30% of its original value. The area of the flat passivated surface at the constriction was measured from oxide replicas of etched surfaces, such as those shown in Fig. 1. The passivated area is given in Fig. 3 as a fraction of the tunnel tip area before the constriction (about 4 μm²). The fractional area is plotted vs. the pulse time. The data show a clear trend of increasing passivation with increasing pulse time, which demonstrates the reproducibility of the tunnel width constrictions. When the current is reduced, surface changes take place which result in increasing passivation with increasing time at the low current. The points at the right of the figure represent current step experiments. The passivated areas for a pulse time of 12 ms are about the same as those in step experiments. Therefore, 12 ms at the low current is the time for the surface changes resulting in the observed passivation in step experiments. Figure 3 shows that pulses of 3 ms or less resulted in no passivation.

It is noted that a maximum of only 40% of the tip area is passivated by the current reduction, but the current was reduced by 70% of its initial value. After the current step experiments, a number of tunnels were present which did not have constrictions, but were significantly shorter than the tunnels with constrictions. Apparently, the current reduction resulted in complete passivation of some tunnels, but only partial passivation of others. The reproducibility of the constrictions shown in Fig. 3 indicates the fraction of tunnels which passivated completely is also reproducible.

Potential transients.—A potential transient for current step reduction experiments is shown in Fig. 4 for the experimental conditions of Fig. 3. Nomenclature to be used below is defined in the figure. Also, a potential transient for a current step at 50 ms etch time is shown. At 50 ms, no tunnels are present, but only cubic etch pits about 0.1-1 μm in depth (15). The repassivation potential of aluminum was measured for the conditions in Fig. 3, by extrapolating to zero current the cathodic scan of a cyclic current-potential curve (potential scan rate 5 mV/s), measured in the potential region in which pitting occurs. The repassivation potential obtained in this manner was ~-0.75V, which is cathodic to the steady-state potentials in Fig. 4.

Figure 5 shows the early portion of the potential transient following a step current reduction, for an experiment with the same conditions as that in Fig. 4a. The potential reaches a minimum at a time of 0.15 ms after the current step. The capacitive current on the Al surface is proportional to the time derivative of the potential; therefore, at
the time of the potential minimum, the capacitive current is zero, so the faradaic current in tunnels has adjusted completely to the reduced applied current. Comparison with Fig. 3 shows that the time of the potential minimum is earlier than 3 ms, the largest pulse time for which no constrictions in tunnels were observed.

These results show that after current steps, the faradaic current is temporarily reduced before the surface changes resulting in permanent passivation take place. However, Alwitt et al. (9) showed that the rates of both anodic metal dissolution and cathodic hydrogen evolution are significant during tunnel etching. It is not clear whether the reduction in faradaic current at the potential minimum was achieved through a decrease in the rate of anodic metal dissolution or an increase in the rate of cathodic hydrogen evolution. The latter reaction can take place away from the dissolving surfaces in tunnels, so an increased rate of hydrogen evolution would not necessarily be relevant to the passivation mechanism.

Current cycling experiments.—Experiments with rapid cycling of the applied current were carried out to determine which of the two faradaic reactions responds to rapid current modulation. In each current cycle period, the applied current was held at 200 mA for 2 ms, and then was reduced by 70% to a value of 60 mA for 2 ms. Current cycling was initiated after a time of 2 s at a constant current of 200 mA, and was continued for the remainder to the etch time, at least 10 s; the time of 2 s at 200 mA allowed growth of tunnels to initiate. The period of 2 s at the reduced current in a current cycle is much larger than the time of the potential minimum after single current steps, which was 130 µs. Thus, it was expected that variations of the current during cycling would be supplied through changes in the faradaic current from the Al foil. If the faradaic current was periodically adjusted by changing the rate of metal dissolution, the weight loss during etching would be affected by cycling. Thus, after the current cycling experiments, the weight losses from the electrodes were determined.

Figure 6 shows scanning electron micrographs of replicas of etched surfaces after experiments both with and without current cycling, but otherwise under the same conditions. The shapes and surface distribution of tunnels and etch pits are the same in the two cases. Thus, the periodic variation of current during cycling is not supplied by repeated nucleation and passivation of etch pits and tunnels; instead, tunnel growth is continuous during the applied current modulation. Continuous tunnel growth is reasonable since Fig. 3 shows that, in single current pulse experiments, a 70% current reduction for a pulse time of 2 ms did not induce permanent passivation in tunnels.

The weight loss from Al foils, in experiments with and without current cycling, is shown in Fig. 7. The weight loss in both cases increases linearly with etch time, and the weight loss in constant current experiments is clearly larger than in cycling experiments. A 35% smaller charge per unit time was applied in cycling experiments as compared to constant current experiments. The solid lines in the figure are the calculated weight losses, assuming the same constant current efficiency of 124.0% for metal dissolution for both types of experiments. This value of the current efficiency was chosen to fit the weight loss data for constant current experiments; current efficiencies of 110-115% during a tunnel etching were reported by Alwitt et al. (9). The good agreement between the calculated and measured weight losses in cycling experiments indicates that the reduced charge per unit time during cycling is supplied by a decreased average rate of anodic metal dissolution, and not by an increased rate of cathodic hydrogen evolution.

Average tunnel growth rates were determined from the lengths of tunnels measured after the experiments in Fig. 6. The average growth velocity for 15 tunnels in current cycling experiments (Fig. 6b) was 1.25 µm/s, as compared to the average growth velocity of 2.04 µm/s for 17 tunnels measured in constant current experiments under the same conditions (Fig. 6a). This 39% reduction in tunnel growth rate during current cycling is in reasonable agreement with Fig. 6b at constant current 0.2 A, followed by repetitive cycling of applied current for remaining etch time (a single cycle is 2 ms at 0.20 A and 2 ms at 0.060 A). Solid lines are weight losses calculated assuming a constant current efficiency of 124.0% for metal dissolution.
ment with the 35% reduction in the applied charge per unit time. The reduction in both weight loss and tunnel growth velocity support the conclusion that, in cycling experiments, the electrode current is modulated by variation of the metal dissolution rate from the tips of tunnels, without permanent passivation of the tip surface.

The results of current cycling experiments indicate that rapid changes in the metal dissolution rate in tunnels occur after step changes in applied current. This result implies that for the current step experiment in Fig. 4a and 5, the metal dissolution current on the tunnel tip is reduced by 70% at a time of 0.13 ms after the step, before surface changes resulting in permanent passivation take place. The effects accompanying this rapid reduction in dissolution current are reversible, since there is no alteration of either the tunnel width or tunnel length if the applied current is returned to its original value within 3 ms after the current step. Even in current step experiments, where the applied current is maintained at the reduced value, the reduction in dissolution current following the step is temporary: Alwitt et al. (9) reported that after the constriction in tunnel width caused by the current step, the tunnel growth rate returns to its original constant value before the step.

The reduction of the dissolution current with a decrease in potential in step experiments does not indicate a general dependence of the aluminum dissolution current on potential. The results of transport model calculations for steady tunnel growth showed that the potential at the dissolving tunnel tip surface decreases continuously with tunnel length, due to the increase of solution phase transport resistance with increasing tunnel length (11). For example, for tunnels at 70°C, the predicted potential (vs. a Ag/AgCl electrode at the tunnel tip) decreases by 25 mV while the tunnel grows to a length of about 20 μm [see Fig. 10 in Ref. (11)]. Despite the decreasing electrode potential at the tunnel tip, the tunnel growth rate measurements in Ref. (13) indicate that the dissolution current density remains constant. Thus, the variation of dissolution current with potential is associated not with steady tunnel growth, but with transient phenomena which precede rapid passivation in current step experiments.

Potentital transient amplitude.—In this section, the potential transients are analyzed to determine the potential change at the metal surface which accompanies passivation. The amplitude of the potential transient is considered as two sequential potential decreases, $\Delta E_1$ and $\Delta E_2$ (Fig. 4). $\Delta E_1$ is the difference between the initial potential and the steady-state potential after the transient, and $\Delta E_2$ is the difference between the steady-state potential and the minimum potential. $\Delta E_1$ and $\Delta E_2$ are considered separately in the following discussion.

Figure 8 shows the dependence of $\Delta E_1$ on the parameter $(i_{a1}-i_{a2})/i$. In obtaining the results shown in Fig. 8, experiments were carried out using values of $i_{a1}$ from 12.9 to 200 mA/cm², and current reductions between 10 and 60%. The etchant solution conductivity was also varied between 0.06 and 0.5 (cm·Ω)⁻¹ by performing experiments in HCl and AlCl₃ solutions of various concentrations. Figure 8 indicates that a linear relationship is followed for all experimental conditions: $\Delta E_1 = (1.15 \text{ cm})(i_{a1}-i_{a2})/i$. This relationship can be rearranged to obtain an equation for the inverse slope of the steady-state current-potential curve: $\varepsilon (dE/di) = 0.227 \text{ cm}^{-1}$. This result can be compared to the current-potential relation that would be predicted if the steady-state current is controlled by the ohmic resistance of the bulk solution. For the primary current distribution, the resistance of a disk electrode with a counter electrode at infinity is given by $R_0 = 1/(4r_0)$ (16). Using $r_0 = 1.27 \text{ cm}$, the radius of the window in the glass electrode holder, $R_0$ is 0.197 cm⁻¹ for the disk electrode. $R_0$ is 13% smaller than the experimental value of $\varepsilon (dE/di)$. The increased resistance of the etching cell relative to the disk electrode can be attributed to the recessed Al electrode and the close proximity of the counter electrode (about one window diameter). It is concluded that $\Delta E_1$ is a change in the ohmic potential drop in the bulk solution due to the reduction in current flow to the counter electrode.

The remaining potential drop $\Delta E_2$ in step experiments is associated with overpotentials of individual pits or tunnels. $\Delta E_2$ may be a combination of changes in the potential drop in the solution in pits and tunnels, and changes in the potential at the metal surface. In order to identify a possible surface potential driving force during passivation, the contribution of transport to $\Delta E_2$ must be evaluated. Solution phase transport processes in tunnels after current step reductions were modeled in Ref. (11). In this model it is assumed that the potential at the metal surface was always at the repassivation potential, so the predicted potential transients reflect only changes in the potential drop in solution in the tunnel due to the current step. The model transients were initiated by a step reduction in the faradaic current at the tunnel tip. The step reduction in the current was followed by an abrupt drop in the predicted potential, caused by the reduced ohmic potential drop in the tunnel. Therefore, the contribution of transport processes to the experimental potential transient amplitude $\Delta E_2$ is through changes in the ohmic potential drop for individual tunnels.

The effect of solution ohmic resistance in tunnels on $\Delta E_2$ is evaluated in Fig. 9 and 10. Figure 9 shows the experimentally determined effect of the tunnel ohmic resistance on $\Delta E_2$. Values of $\Delta E_2$ for 40% current step reductions at
various etch times are plotted. The abscissa is \( t \), where \( n \), the tunnel growth velocity, is 2.1 \( \mu \text{m/s} \). This value was obtained using the superimposed ac technique of Hebert and Alkire (13); no variation of the growth velocity with tunnel length was detected. Results for small etch pits and for tunnels are shown. The slope of the line drawn in the figure is \( 0.41b/k \), where \( i_0 \) is the tunnel current density, is 6.1 A/cm\(^2\). \( b \) is 0.1 (\( \Omega \text{-cm} \)) \(^{-1}\), a representative conductivity for the solution in the tunnel (17). This line represents the expected contribution of ohmic potential drop in tunnels to \( \Delta E_2 \). Figure 9 shows that the variation of \( \Delta E_2 \) with tunnel length can be attributed to the ohmic resistance of tunnels. The intercept is \( \Delta E_2 \) for the small etch pits present at early times, and is also a contribution to \( \Delta E_2 \) for tunnels which is independent of tunnel length.

The intercept in Fig. 9 is now compared to the expected ohmic potential drop in pits. The magnitude of the ohmic potential drop for small cubic etch pits is estimated using a solution of Laplace’s equation for a hemispherical pit with uniform current density, on an insulating plane (18). This calculation includes the resistance of the solution outside the pit. The ohmic potential drop is given by

\[
\eta_{op} = \frac{3 \pi d}{K} k
\]  

[1]

Pit size distributions were measured by Wiersma and Hebert (15) for anodic etching in 1N HCl at 65°C at etch times less than 100 ms. The root mean square pit depth was 0.20 \( \mu \text{m} \). Also, these authors concluded that the current density in these pits was about 6 A/cm\(^2\), the same as in tunnels at these etching conditions. With \( r = 0.2 \mu \text{m} \), \( i_0 = 6 \text{ A/cm}^2 \), and \( k = 0.5 \text{ (\Omega-cm)}^{-1} \) for 1N HCl at 65°C (19), \( \eta_{op} \) is about 0.7 mV, which is much smaller than the intercept in Fig. 9.

On the other hand, if there are obstructions such as gas bubbles in pits, the ohmic potential drop could be much larger than indicated by Eq. [1]. According to Pickering and Frankenthal (20), large potential drops in pits are caused by gas bubbles within the pits. Sides and Tobias (21) showed that when a layer of bubbles is present on an electrode surface the ohmic potential drop to the electrode is increased by a factor of five; the ohmic drop due to the bubbles is inversely proportional to the conductivity of the solution around the bubbles. The ohmic potential drop could also be greater than that calculated above if the dissolution current density is much larger than the value of 6 A/cm\(^2\) obtained by Wiersma and Hebert. In this case, the ohmic potential drop for the pit would also be inversely proportional to the solution conductivity.

The dependence of \( \Delta E_2 \) on etchant solution conductivity for small pits is shown in Fig. 10. The conductivity variation in the figure is for 0.1-1.0M HCl solutions and 1-9N AlCl\(_3\) solutions. The figure shows that \( \Delta E_2 \) is independent of bulk solution conductivity. Because of the higher concentration in the pit relative to the bulk solution, the conductivity in the pit would be displaced from that of the etchant solution (22), but there should still be significant variation of the pit conductivity as the AlCl\(_3\) concentration varies from 1 to 9N. The absence of dependence of \( \Delta E_2 \) on solution conductivity thus indicates that this potential drop is not due to an ohmic resistance. It is concluded that \( \Delta E_2 \) is a reduction in the potential at the metal surface preceding passivation. Also, since, if bubbles were present, the effect of solution conductivity on \( \Delta E_2 \) would be noticeable, Fig. 10 further shows that there are no such obstructions in the pits. For the same reason, Fig. 10 indicates that the pit current density is not appreciably higher than the value of 6 A/cm\(^2\) determined by Wiersma and Hebert (15).

The dependence of \( \Delta E_2 \) on the percent current reduction and the initial current level in current step experiments are shown in Fig. 11. The results show that \( \Delta E_2 \) is approximately linear in the percent current reduction. Figure 11 indicates an approximately linear relation between the faradaic current and surface potential

\[
i = i_0(1 + k(E - E_0))
\]  

[2]

\( i \) and \( i_0 \) in Eq. [2] are average faradaic current densities on the corroding surface, referred to the total active area before passivation. \( \Delta E_2 \) should not depend on applied current because it is a potential change associated with individual pits. However, \( \Delta E_2 \) values for the three larger applied current densities fall on a line with a 30% higher slope than for the applied current density of 12.9 mA/cm\(^2\). It is shown in the next section that at the lower applied currents the potential decreases to the minimum potential much more slowly than at the high currents. It is possible that for the low currents, processes which operate at long times cause the smaller value of \( k \).

Figure 11 shows that \( \Delta E_2 \) is a change in the potential at the metal surface which is associated with a rapid reduction in the metal dissolution current on the corroding surface preceding passivation. But \( \Delta E_2 \) is \( E_0 - E_{\text{min}} \), where \( E_0 \) is the steady-state potential after the transient, and \( E_{\text{min}} \) is the minimum potential (see Fig. 4). The repassivation potential is usually measured by extrapolating the steady-state current-potential curve in the pitting region to zero current (23). But in the present work, the current-potential curve during pitting is determined by bulk solution ohmic resistance. Thus, the potential obtained by extrapolation of the steady-state current-potential curve to zero current is also the potential at the metal surface during etching. For this reason, the repassivation potential is also the potential at the surface at steady state; that is, the surface potential when the measured potential is \( E_{\text{cor}} \). \( E_{\text{min}} \) differs from...
the potential at the surface at the time of minimum by the same constant bulk solution ohmic potential drop as that present after the transient. Therefore, $\Delta E_c$ is equal to the surface overpotential relative to the repassivation potential. It is concluded that the driving force for the changes in metal dissolution current before passivation is cathodic overpotential relative to the repassivation potential at the metal surface.

Kinetics of reduction of faradaic current.—In this section processes which determine the time dependence of the potential decrease to the minimum potential are discussed. A simple model for the potential decrease from $E_o$ to $E_{\text{min}}$ was formulated which considers that the time variation of potential is controlled by capacitive discharging. This assumption implies that as the potential decreases through $\Delta E_c$, the faradaic discharge immediately at every potential to the value given by Eq. [2], there is no delay associated with kinetic processes on the surface. For example, rapid adjustment of the surface to new compositions, without kinetic activation, is associated with adsorption phenomena.

The differential equation describing the decrease of the potential from $E_o$ to $E_{\text{min}}$ is

$$i_a = C_d \frac{dE}{dt} + \left( nA_i \phi /c \right) \left[ 1 + k(E - E_o) \right]$$

Equation [3] is a current balance; the first term on the right is the capacitive charging current, and the second term on the right is the metal dissolution current from pits. The dissolution current term contains the dependence of current on potential indicated in Eq. [2]. The factor $(nA_i \phi /c)$ is also the applied current before the step, $i_a$. Equation [3] assumes that the potential derivative on the surface being discharged is the same as the derivative of the experimentally measured potential. This assumption is reasonable for surfaces containing only small etch pits, because the calculation and discussion following Eq. [1] show that the potential drop associated with these pits is on the order of 1 mV, and thus variations of the potential along the etched surface are small. The initial condition for Eq. [3] is that $E = E_o$ when $t = 0$, the time of the current step.

The solution to Eq. [3] is

$$(E_{\text{min}} - E)(E_{\text{min}} - E_o) = \exp \left[ -(i_a k/C_d) t \right]$$

In writing Eq. [4], it is assumed that the potential at infinite time predicted by the model is the same as the potential at the minimum of the transient, $E_{\text{min}}$. This assumption implies that the electrode surface is completely discharged, before the initiation of the processes which cause the potential to increase after the minimum. The dependence of the dimensionless potential in Eq. [4] on time is shown in Fig. 12. The exponential decay predicted by Eq. [4] is followed, and there is no dependence on the percent current reduction.

Figure 13 shows the dependence of the exponential decay slope on initial applied current and percent current reduction. Solid line is theoretical slope calculated from Eq. [4] with $C_d = 11.6 \mu F/cm^2$, $k = 5.98 V^{-1}$. Etch time 50 ms, etchant solution 1N HCl.

$$S = \frac{1}{9.0 \times 10^{-10}} \times k \left( \frac{200}{i_a} \right)^2$$

Potential relaxation to steady state.—Figure 14 shows the dependence of the time for potential increase from $E_{\text{min}}$ to $E_o$ on etch time, for 40% current reductions. Results

![Fig. 12. Exponential decay of dimensionless potential after step reduction in current. Initial applied current density 60 mA/cm². Origin of the time scale at the step time. Current reductions: 10, 25, 40, and 50%. Etch time 50 ms, etchant solution 1N HCl.](image)

![Fig. 14. Dependence of exponential decay slope $S_i$ for potential transients on etch time at the step. $v$ is tunnel growth velocity. Solid line represents solution diffusion contribution to relaxation time. 40% current reductions. Etchant solution 1N HCl, applied current density 60 mA/cm², temperature 65°C for this work; 1N AlCl₃, 10 mA/cm², 70°C from Hebert and Alkire (11).](image)
from the present work for small pits (1N HCl solution) are shown along with results for tunnels (1N AICl solution) from Ref. (11). The ordinate on the figure is $S_{1/2}$, where $S_{1/2}$ is the slope of the plot of $\ln(E - E_m)/\Phi$ vs. time, at time $t$. The abscissa is $vt$, where $v$ is the tunnel growth velocity, $1.6 \mu m/s$ for the foil in this work. The slope of the line drawn in the figure is $10^{-3} \pi (2D)^{-1} \pi^{1/2} \mu m$. $D$ is the diffusivity of the AICl electrolyte; Hebert and Alkire (11) modeled the solution in the tunnel as a binary AICl electrolyte solution. The value of the diffusivity in Fig. 14 is $2.1 \times 10^{-5} \ cm^2/s$, reasonable for AICl. Any possible infinite dilution is $2.7 \times 10^{-5} \ cm^2/s$ (11). The model for transport in tunnels in Ref. (11) predicted that $S_{1/2}$ should be directly proportional to tunnel length: $S_{1/2} = L/(2.4D)^{1/2}$. The experimental results in Fig. 14 follow this dependence, except for a nonzero intercept for zero tunnel length; it is concluded that the potential decay time is partly determined by solution diffusion.

The intercept at zero tunnel length can be used to determine a relaxation time for tunnels which is not affected by diffusion. The time for 80% decay of the potential transient, determined in this way, is 40 ms. This time is much longer than the current pulse time of 12 ms (Fig. 3) for complete passivation in 70% current reduction experiments. Thus, the potential decay time for tunnels is much longer than would be expected from solution diffusion, in combination with the current pulse times for passivation. The reason for this extended potential decay time cannot be determined at the present time.

Figure 14 also shows potential decay slopes for experiments at early times for which only small etch pits are present. A potential transient for these times is shown in Fig. 14 for 50 ms etch time, the decay time is about 5 ms. This time can be compared to the diffusion time constant for small pits, $\pi (2D)$. Using $2.1 \times 10^{-5}$ cm$^2/s$ for $D$ (see above) and 0.2 $\mu m$ for $r$, the constant is on the order of $10^{-5}$ s. Therefore solution-phase diffusion does not influence the potential relaxation time for small pits; instead, the potential decay may be related to passivation kinetics. Figure 14 shows that the potential decay times, exclusive of diffusion effects, become longer as the etch time increases, and the primary corrosion structures on the surface shift from pits to tunnels. This increase in the decay times is correlated with the appearance of constrictions in micrographs. For the 40% current step reductions, there were constrictions in nearly all tunnels on the surface for etch times greater than 1.58 $\mu m$; some constrictions were visible after the 0.5 $\mu m$ (vt = 1.05 $\mu m$) etch, and there were no constrictions for etch times smaller than 0.5s. The longer potential decay time for growth times greater than 0.5 $\mu m$ may be related to the type of passivation giving rise to constrictions.

Conclusions

Passivation of corroding surfaces in aluminum etch tunnels was observed using scanning electron microscopy. Microscopy allowed direct observation of passivation. Radiant passivation was induced through step reductions in applied current, as well as cathodic current pulses. The potential transients accompanying the experiments were analyzed to identify the driving force for passivation. After step decreases in current, the potential falls rapidly as the electrode discharges; the charging time for adjustment of the faradaic current to the new applied current is 0.13 ms for the experimental conditions of this work. Experiments with cycling of the applied current showed that the adjustment of faradaic current occurs by reducing the metal dissolution rate in tunnels. This reduction of dissolution current with decreasing potential is not observed during steady tunnel growth; it is associated with transient events preceding steady tunnel growth. The decrease in the dissolution current at the charging time is proportional to the cathodic surface overpotential relative to the repassivation potential.

The decrease in the dissolution current before passivation is reversible, since no change in tunnel width is observed if the applied current is returned to its original value within 3 ms after the step. Current pulse experiments showed that the surface changes resulting in permanent passivation occur later than 5 ms after the current step reduction. For 70% step current reductions, the surface changes resulting in passivation are completed after 12 ms.

The results imply that at the charging time, the corroding surface has changed to a state which is a precursor to permanent passivation, but this change can be reversed by increasing the current. The dependence of this surface change on cathodic deviations from the repassivation potential indicates the importance of controlling passivation on the corroding surface. This investigation has shown that the events during passivation may be complex, and more detailed study is necessary before a model for passivation is formulated.

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LIST OF SYMBOLS

$A$ area of electrode surface, 5.07 $\cm^2$
$A_p$ average active area in pits, $\cm^2$
$C_d$ differential capacitance of Al surface, $F/cm^2$
$D$ diffusivity of binary electrolyte, $\cm^2/s$
$E$ potential measured during etching experiments, $V$
$E_m$ minimum potential in transients, $V$
$E_s$ steady-state potential after current step transients, $V$
$i$ average faradaic current density in pit or tunnel, referred to active area, $A/cm^2$
$i_c$ applied current density before step change in current, $A/cm^2$
$i_d$ applied current density after step change in current, $A/cm^2$
$i_m$ metal dissolution current density in pits or tunnels, $A/cm^2$
$i_o$ average faradaic current density in pit or tunnel, at potential $E_o$, referred to active area, $A/cm^2$
$k$ proportionality constant between $(E - E_o)$ and fractional reduction in metal dissolution current density, $V^{-1}$
$L$ tunnel length, $\cm$
$n_p$ surface density of pits and tunnels, $\cm^{-2}$
$R_o$ ohmic resistance, $\Omega$
$r$ pit depth, $\cm$
$r_e$ radius of disk electrode, $\cm$
$S$ slope of logarithm of potential $\Delta \Phi$ vs. time during potential relaxation after current step, $1/s$
$t$ time, $s$
$\Delta \Phi$ discontinuous potential change after current steps, $V$
$\Delta \Phi_o$ total potential drop in potential transients, in excess of the initial discontinuous potential change, $V$
$c_e$ current efficiency for metal dissolution
$\kappa$ solution conductivity, $(\Omega \cdot cm)^{-1}$

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Nonuniform Distribution of Current and Potential on Al Specimens Polarized in NaOH

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ABSTRACT

In an earlier paper (6) we have presented evidence of the nonuniform distribution of current and potential on AlSn specimens polarized in NaOH. By combining microscopic observations and electrochemical measurements we have previously concluded inferentially that local potentials on polarized electrodes can differ substantially (several hundred mV) between the center and the edge of a specimen. In this paper we were able to prove experimentally that such nonuniform distributions of the potential and the current do exist. Results of potentiostatic and potentiodynamic experiments with Al in 0.1M NaOH are presented. The potential differences between center and edge were found to be influenced by the geometry of the specimen. This dependency in return influences the integral current and hence the shape of current density/potential plots in an unpredictable way. A particular specimen arrangement in conjunction with a low impedance measuring device for divided currents added to a conventional potentiostat is proposed to eliminate the distorting effects on electrochemical measurements caused by the nonuniform potential distribution.

In analogy to heat conduction, Newman (1) has calculated the theoretical or primary distribution of the current flow to a circular electrode. The current density (CD) is shown to increase with increasing lateral distance from the center of the disk and to approach infinite values at the edge. Because of the polarization of the specimen and the restriction in mass transfer caused by convection and diffusion, the CD will be limited to finite values at the edge. The resulting secondary current distribution is a complicated function of the electrochemical behavior of the system under investigation and the geometrical environment of the cell. It can, at best, be predicted semiquantitatively if the potential/current density curve (E/i curve) is known. To quantitatively assess the extent of this nonuniform distribution experimental techniques must be employed.

The extent of such secondary current and potential distributions and the influence on electrochemical reactions has been investigated earlier. Miller and Bellavance (2) have employed several techniques to assess the current distribution at rotating ring disk electrodes (RRDE) and have found quantitative agreement with the predictions of Newman (3). They also report of collection efficiencies at RRDE to be in qualitative agreement with the expected current distribution. Baizer et al. (4) report the nonuniform potential distribution at the cathode to be a potential problem in the reductive coupling of activated olefins. Competitive reduction reactions can take place simultaneously on the electrode because their potentials are less than 200 mV apart. Using a multi-Luggin probe arrangement, Mears and Rothwell (5) have found that electrode geometry strongly influences the potential distribution on the anode.

In an earlier paper (6) we have shown ring-shaped structures that develop visibly on the surface of heterogeneous alloys of Al-10 volume percent (v/o) Sn in 0.1M NaOH and a technical aluminum bronze in 0.05M NaCl, which are due to the nonuniform potential distribution. In the paper presented here we have investigated experimentally the degree of the nonuniform distribution of the CD and the potential on pure aluminum electrodes in sodium hydroxide solutions. These nonuniformities in return have an influence on the shape of conventionally obtained E/i curves.

Experimental

Aluminum [99.99 weight percent (w/o), major impurities Fe, Si, and Cu] was melted under vacuum in an induction furnace and cast into a graphite crucible. Samples approximately 25 mm long with various cross sections (Fig. 1) were machined from the ingot and embedded in resin. The surfaces of the specimens were finished by polishing with 3 μm diamond paste. To make possible separate measurements of the current passing through the inner and outer portion of a circular specimen, a hollow cylinder and a core (Fig. 1h and 2) were electrically isolated from each other by a layer of resin and had separate electrical conduits. An electronic device to measure parallel partial currents designed by Fa. Jaisse Elektronik, Waiblingen (Germany) was added to the standard Model 60-TB potentiostat of this company (schematic, Fig. 5). Because of its low entrance resistance of <10⁻⁴ the measurements

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Fig. 1. Geometry and arrangement of specimens. (a) to (g): diameter: 1.1, 1.5, 8, 11.3, 13.8, 16, 17.8 mm (1, 20, 50, 100, 150, 200, 250 mm²); (h): divided specimen: 17.8 mm od and 6 mm id for the ring and 5 mm od for the center (cross section see Fig. 2); (i) rectangular shape of 17.8 × 4.5 mm.