Interpretation of Potential Transients during Aluminum Etch Tunnel Growth in the Presence of Sulfuric Acid

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When sulfuric acid is added in an etching solution of 1 M hydrochloric acid, the effect of the sulfate ions on the aluminum etch pit formation and tunnel growth was investigated with the morphology study and current interruptions in applied etching current. Initial potential transient supports that sulfate ion works as a film forming agent and inhibits the pit initiation during the anodic current etching. Observation of ruptured oxide films suggests that cathodic hydrogen evolution can take place inside the pits. Current step reduction and cathodic pulse superimposition experiments indicate that the actively dissolving tunnel tip surface is covered with aluminum chloride salts and sulfate ion moves far behind inside tunnels during the tunnel growth.

Key Words: Aluminum Etching, Potential Transients, Passivation, Current Interruption Method

1 Introduction

Pitting is a common observation in aluminum corrosion. Aluminum pits show a unique geometry as a result of anodic etching in hot HCl solution. Cubic etch pits are initially formed in the early stage of etching and become tunnel-like structure after etch times of several seconds. Tunnels grow along <100> crystallographic directions and growth velocities are several μm per second with a 1-4 μm width. As temperature increases, the tunnel growth rate increases. Electrochemical tunnel etching of aluminum has been used for manufacturing an aluminum electrolytic capacitor to create a high surface area. Surface area of aluminum is closely related with tunnel morphology, which depends on microstructure of the aluminum and etching conditions.

For high voltage applications, high-purity aluminum foil is dc etched in the sulfate-containing hot hydrochloric acid solution. Sulfate ion is used as an oxide forming agent at low temperature. Sulfate ion has competitive adsorption with chloride ion and pushes the pitting potential towards positive potentials. This effect causes the morphological change of etched tunnels; increase of sulfate concentration increases tunnel density but decreases the maximum tunnel length. Tapering of tunnel is also observed in higher concentration of sulfuric acid. Pyun et al. suggested that sulfate ion has the aggressive nature for the pit growth above pitting potential at 60°C and 80°C.

In this work, the effect of sulfate ion on the aluminum etch pit formation was investigated with the morphology study by using a scanning electron microscopy and potential transient analysis. Current interruption experiments were designed to induce the passivation during aluminum etch tunnel growth and the measured potential variations were interpreted to elucidate the role of sulfate ion during the etch tunnel growth.

2 Experimental

The electrochemical cell body is consisted of a glass cylinder capped with a Teflon lid holding all three electrodes. The polycrystalline aluminum foil (capacitor grade 99.99%, Tokai, Japan) of 104 μm thickness was used as the working electrode (WE). The geometric area of an electrode during etching was 1 cm². Prior to the etching experiment, the aluminum foil was chemically treated in 1 M HCl at room temperature for 3 min and then rinsed in deionized water. A platinum wire was used as a counter electrode (CE) and Ag/AgCl/4 M KCl was employed as a reference electrode (RE). RE was placed behind the WE holder. HCl and H₂SO₄ (Aldrich, analytical grade) solutions used in this study were prepared with deionized water (Millipore, 18.2 MΩ cm). Experiments were carried out at 65°C in stirred solution.

Applied current waveform was modulated and supplied by a potentiostat/galvanostat (EG&G PAR 273 A) interfaced to an IBM compatible computer. Accompanying potential transients were measured with a digital oscilloscope (TDS 350). Tunnel morphology was investigated by scanning electron microscope (SEM, Hitachi X-650) and the surface composition was analyzed by Auger electron spectroscope (AES, PHI 600).

3 Results and Discussion

3.1 Effects of sulfate ion on the pit formation

Figure 1 shows the potential transients when anodic current of 40 mA cm² is applied with the variation of sulfuric acid concentration. The rapid increase of initial potential falls on the same transient and it increases slowly to peak potential, Eₚ, then returns to the steady-state anodic potential, E₀. Both the peak potential and the potential decay time, τ₀, from Eₚ to E₀ increase with H₂SO₄ concentration, as shown in Fig. 2. Considering τ₀ is a period of time needed for chloride ion to reach the metal/
Fig. 1 Initial potential transients for different concentrations of H₃SO₄. (a) 1 M HCl, (b) 1 M HCl + 1 M H₂SO₄, (c) 1 M HCl + 2 M H₂SO₄, (d) 1 M HCl + 3 M H₂SO₄, (e) 1 M HCl + 4 M H₂SO₄. Anodic current = 40 mA/cm², Temperature = 65°C.

Fig. 2 Variation of potential increase $\Delta E_{\text{max}}$ and decay time $\tau_0$ for different concentrations of H₃SO₄.

oxide interface, potential increases to $E_{\text{pp}}$ can be interpreted with the anodic oxide film formation process. Figure 3 shows the potential increase when aluminum is anodized in H₂SO₄ only solution at 65°C with 40 mA/cm². After a sudden potential rise due to ohmic drop and double layer charging, potential increases at a rate of 3.8 V/s as the oxide film is thickened. It is commensurate with the film growth rate of 2.7 nm/s since potential increases by 1.4 V/nm. In the slow potential increase region of Fig. 1, etch pits are not found and average film growth rate is measured at 2.9 nm/s, similarly to 2.7 nm/s in H₂SO₄ only solution. The results suggested that the potential increase to $E_{\text{pp}}$ can be attributed to the general oxidation of filmed surface and the thickness of films increases with increasing H₂SO₄ addition. Thickening of the oxide film increases the potential decay time, $\tau_0$, by requiring the longer penetration length of chloride ion through films. Pits are initiated during the potential drop from $E_{\text{pp}}$ to $E_{\text{a}}$. The remaining surfaces are covered with sulfate-included oxide films and these are visible after etching of 10 s. It will be discussed later in morphology studies.

Inhibiting behavior of sulfate ions for the pit formation is investigated in hot HCl solution. Figure 4 shows linear sweep voltammograms in 1 M HCl solutions with the variation of H₂SO₄ concentration. H₂SO₄ addition moves pitting potential to the anodic direction by suppression of pit initiation. At more anodic potentials above pitting potential, anodic current increases with the increasing H₂SO₄ solution and it suggests the possible aggressive behavior of sulfate ion for the bare aluminum dissolution. On the other hand, addition of Na₂SO₄ induces inhibiting behavior over entire potential scan range. Above the pitting potential, the effect of sulfate ion remains less clear because of its complex behavior. However, since aluminum/aluminum oxide becomes unstable at low pH, it can be assumed that pH of the solution is more responsible than sulfate ion for the current increase above the pitting potential.

Figure 5 shows the surface of aluminum specimen produced in which anodic current of 40 mA/cm² was applied for 10 s. Low magnification images indicate that, with increasing H₂SO₄ concentration, pit density increases and the average pit size diminishes, as observed in other works. In HCl only solution, number of pits are interconnected and have sharp edge lines of which reflects the etched surface. However, close examination of pits discloses the existence of oxide film over the pit mouth when sulfuric acid is added. When 1 M H₂SO₄ is added, edges of pit mouth are not clearly shown due to oxide debris formed by the mechanical rupture (arrow in Fig. 5). Since current efficiency during tunnel etching is 110-115%, cathodic hydrogen evolution may be responsible for the oxide rupture. In case of 2 M H₂SO₄ addition, a number of pits are found underneath oxide films and parts of pitted area are repassivated (circle in Fig. 5),
that is, oxide formation effect becomes more pronounced. AES depth profile of Fig. 6 indicates the inclusion of sulfate ion in the oxide film. These results suggest that sulfuric acid have a significant influence on the oxide film formation during the anodic etching in hot HCl solution.

3.2 Effects of sulfate ions on etch tunnel growth

Tunnels are the dominant structure on aluminum surfaces during the anodic etching in a sulfate-containing hot HCl solution. The tunnel tip surface dissolves actively and remains a flat surface but its wall surface remains passive, during the etch tunnel growth. Current step reduction induces the passivation of actively dissolving tunnel tip surface and tunnel tip area is reduced. Figure 7 shows the applied current waveform for current step reduction and the accompanying potential transients after 5 s of the anodic etching are shown in Fig. 8. In 1 M HCl + 2 M H$_2$SO$_4$ solution, potential decays rapidly to the minimum potential after the step and has a slow increase to steady potential at $i_{d}/i_{a} = 0.75$ and 0.5. At reduced current, $i_{d}$, steady potential is the repassivation potential. Below the repassivation potential, corroding surfaces are passivated. During potential relaxation from the minimum potential to steady potential, tunnel tip surface remains below repassivation potential and parts of actively dissolving areas are passivated. However, potential overshoot is suddenly appeared when the current reduction ratio is 0.25. Figure 9 shows that, with increasing H$_2$SO$_4$ concentration, potential overshoot size increases but the time to reach peak potential decreases. When potential overshoot is absent, tunnel tip surface experiences the morphology changes of which number of actively dissolving patches become a single patch during the potential relaxation. Potential overshoot is related with the behavior of the oxide film present at the metal surface and the pit formation, as discussed in Fig. 1. Therefore, passivation of the entire tip surface and the following pit initiations cause the overshoot during potential relaxation, at higher H$_2$SO$_4$ concentration with $i_{d}/i_{a} = 0.25$. Considering the presence of the adsorbed chloride salt layer on the actively dissolving tip surface, current step reduction causes the backward diffusion of chloride ions which exists on the passivating areas. Simultaneously, sulfate ion near tip surface moves to the tunnel mouth and the ratio of sulfate to chloride concentration near the tip surface can be changed. Since both the size and charge of sulfate ion are greater than chloride ion, diffusion velocity of sulfate ion is expected to be slower and it will result in the increase of sulfate/chloride concentration ratio near tip surface. Because a large fraction of the tip surface is passivated at higher current.
Electrochemical etching of aluminum in hydrochloric acid solution is greatly influenced by the addition of sulfuric acid. This work investigated the effect of sulfuric acid addition on the initial pit formation and pit growth and, the following conclusions were drawn.

1. When 40 mA/cm² of anodic etching current is applied, the anodic film growth is preceded before etch pits are initiated. Film growth rate is estimated at about 2.7 nm/s, independently of H₂SO₄ concentration. However, with increasing H₂SO₄ concentration, thick anodic oxide film is formed on the aluminum surface and it retards the pit initiation.

2. After 10 s of anodic etching in sulfate-containing solution, anodic oxide films were locally found on the pit mouth and, in part, mechanically ruptured films were also observed. Cathodic hydrogen evolution underneath the film is considered as a possible cause for the film cleavage. Above the pitting potential, sulfate ion show complex behavior on metal dis-

![Fig. 8](image1.png)

**Fig. 8** Potential transients for fractional current reductions. Etching solution; 1 M HCl + 2 M H₂SO₄, Current density = 40 mA/cm², Temperature = 65°C.

![Fig. 9](image2.png)

**Fig. 9** Potential transient for fractional current reductions. Basis = 1 M HCl solution, Variables = H₂SO₄, Concentration : (a) 1 M H₂SO₄, (b) 2 M H₂SO₄, and (c) 3 M H₂SO₄. Temperature = 65°C.

![Fig. 10](image3.png)

**Fig. 10** Applied current shape for current pulse experiments. Variables ; i₁, i₂, t₁.
solution current and this may be caused by the substantial decrease of solution pH with H$_2$SO$_4$ addition.

(3) Current step reduction and cathodic pulse is superimposed in anodic current etching. At higher current reduction ratio, higher H$_2$SO$_4$ bulk concentration can only induce the passivation of actively dissolving tip surface within 0.5-1 s of time span, despite of the continuing supply of anodic current. Current pulse experiment indicates that the actively dissolving tunnel tip surface is completely covered with aluminum chloride salts. These results indicate that sulfate ions move far behind inside tunnels during tunnel growth.

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