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Pit growth behaviour of aluminium under galvanostatic control

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ABSTRACT

The pit growth process on (1 0 0) aluminium under anodic pulse current in a mixed solution of 1 M HCl and 0.1 M H_2SO_4 at 30 °C has been evaluated using potential transient measurements and pit size distributions obtained by scanning electron microscopy. Sustained pit growth is observed for all pits during the initial anodic potential rise before reaching a steady-state etch potential, whereas a substantial fraction of the pits passivate at the steady-state etch potential. The pit growth rate during the initial potential rise is 3.4 $\mu m\ s^{-1}$, which is similar to that at the steady-state etch potential. The growth rates of active pits are potential-independent.

1. Introduction

Electrochemical etching of aluminium has been employed in the production of high surface area electrodes for aluminium electrolytic capacitors, where the surface area of the electrodes is enhanced due to local attack of a passivated aluminium surface in chloride-containing electrolytes during the etching process [1–9]. The etching of aluminium is still actively studied in recent years to control the nucleation and growth of pits more precisely [10–18]. Electrochemical etching is performed using two types of etch processes, i.e., AC and DC etch processes. Aluminium foil etched by the AC process is typically used for low-voltage capacitors, in which each anodic half-cycle produces a high density of crystallographic pits and ‘pit-on-pit’ propagation during successive cycles creates an ‘etched layer’, a deep layer of porous aluminium with sub-micrometre texture [19,20]. The AC etch process can increase the specific surface area of a smooth aluminium foil by up to a factor of 200. The aluminium foil etched by the DC process is typically used for high-voltage capacitors. The DC etch process produces crystallographic etch tunnels that are $\sim$1 μm wide, up to 50 μm in length, and $10^7\ cm^{-2}$ in pit density [21–23]. The specific surface area of DC-etched aluminium foil is typically 20× that of plane aluminium foil.

Aluminium dissolution occurs preferentially in the $\langle 1\ 0\ 0 \rangle$ direction during the electrochemical etch processes, and thus, the basic structural unit of the porous layer formed by the AC etch process is a half-cubic pit. In the DC etch process, the pit walls of the half-cubic pit passivate within the order of 100 ms, while the pit base continues to dissolve. Pit nucleation and growth are essential steps in both AC and DC etch processes. Pit development has been observed as a part of each process during in-depth examinations [24,25]. However, only a few studies have focused exclusively on the events during the brief interval before tunnels initiate [26,27]. Pit growth rates have been estimated from the increase in the largest pit size at each anodic pulse interval [28], the increase in the average pit size [27,29], or the increase in the mean square pit size [26,30]. The growth rates estimated from the size of the largest pits are much greater than those estimated from the latter two methods. Based on this fact, it was concluded that there are substantial differences between pit growth and tunnel growth at the steady-state etch potential [28].

Initial application of a constant anodic current always produces an anodic potential transient, i.e., a potential rise which precedes a steep drop to a steady-state etch potential. The duration of the potential rise is typically 10–100 ms and is dependent upon the specimen’s thermal and chemical history. It has been reported that growth of an anodic barrier oxide and uniform Al dissolution proceed in parallel with pitting during the potential rise prior to the potential drop to a less noble steady-state potential [24,31]. However, with the exception of the fact that hemispherical pits grow during the potential rise interval, the details of the pit growth behaviour during the potential rise are yet to be clarified [27]. This study focuses on the differences in the growth behaviour of pits during the initial potential rise and the subsequent steady-state etch potential in order to provide further insight into the AC etch process of aluminium.

2. Experimental

The aluminium specimens used in this study were 115-μm-thick, 99.99% pure, fully annealed, electrolytic capacitor grade foil,

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with a high cubicity texture, i.e., more than 90% of the surface was in the (1 0 0) orientation. In general, the foil with a high (1 0 0) orientation is fabricated through several stages of thermo mechanical processing: casting, homogenising, hot rolling, quenching, cold rolling, annealing, and final cold rolling. The foil is then fully annealed in order to complete the re-crystallization process. The aluminium foil used in this study contained 58 ppm copper, 13 ppm silicon, and 10 ppm iron as the prominent impurities, where the impurity concentration is given in ppm by weight. The foil was cut into a rectangular shape with dimensions of 13 cm × 3 cm and covered with an insulating tape except for a 4 cm × 2.5 cm area, which was left open for etching. The foil was pre-treated in 1 M NaOH at 60 °C and then immersed in 1 M HNO_3 at 60 °C for various time periods. Following pre-treatment, the specimen was mounted on a polycarbonate holder having an exposed area of 4 cm × 2.5 cm and transferred into a cell containing 1 M HCl + 0.1 M H_2SO_4 etchant at 30 °C. A current of 100 mA cm^{-2} was then applied using a potentio/galvanostat (Princeton Applied Research, 263A). The counter and reference electrodes were a carbon plate and Ag/AgCl/sat.KCl electrode, respectively.

The surface of the etched foil was observed using a Hitachi, S-4700 field emission–scanning electron microscope (SEM), and the pit size was measured from the SEM images. Pit size refers to the width of a square pit or the diameter of a circular pit. The pit size distributions were determined by image analysis of the plane view of the etched surface using 5000× magnification SEM images. Approximately 200 pits were typically counted for each sample. Prior to SEM observations, the etched specimens were immersed in 0.5 M H_3PO_4 + 0.2 M CrO_3 solution at an elevated temperature of 85 °C for 10 min to dissolve the corrosion product that formed during the etch process.

3. Results

It is known that the duration of the initial potential rise during anodic pulse current application is dependent on the current density [32], pre-treatment conditions [26,33], and the concentration of H_2SO_4 in the etch bath [34]. Fig. 1 shows the effect of immersion time in 1 M NaOH pre-treatment solution on the anodic potential transient in a mixed solution of 1 M HCl and 0.1 M H_2SO_4. It was observed from repeated experiments that the average dissolution rate of aluminium foil in 1 M NaOH at 60 °C, estimated from weight loss measurements, was 35 nm s^{-1}. During this pre-treatment process, the dissolution of aluminium proceeds through the residual oxide film present on the surface [35], and this leads to relatively uniform dissolution without crystallographic attack of the aluminium. Fig. 1 shows that the duration of the initial potential rise preceding the sharp drop to the steady-state potential, is markedly dependent on the immersion time in 1 M NaOH, decreasing from 93 ms to 13 ms as the immersion time is increased from 0 s to 120 s. Because the durations before and after reaching the steady-state potential during the anodic current pulse for 100 ms are comparable for the specimen immersed in 1 M NaOH for 60 s (Fig. 1), this pre-treatment immersion condition, i.e., 1 M NaOH at 60 °C for 60 s followed by immersion in 1 M HNO_3 at 60 °C for 180 s, was considered for a more careful study in order to elucidate the pit growth behaviour. Fig. 2 shows the chronopotentiograms for various durations of the anodic current pulse. The duration of the period before the steady-state potential is reached is 40–50 ms. The grey line in Fig. 2 shows the potential increase when aluminium is anodized in HCl-free 0.1 M H_2SO_4 solution at 30 °C. The linear potential rise appears to indicate constant thickening of an anodic oxide film. The potential rise during the initial 10 ms in a mixed solution of 1 M HCl and 0.1 M H_2SO_4 perfectly traces the potential rise line in the HCl-free 0.1 M H_2SO_4 solution. After 10 ms, the rate of the potential rise in the mixed solution gradually gets smaller.

The change in open circuit potential immediately after termination of the anodic pulse current is also shown in Fig. 2. There are two types of open circuit potential transient, depending upon the duration of the anodic pulse. When the anodic pulse is applied up to the sharp drop of the potential, i.e., ⩾40 ms, a negative potential peak of −1.2 V vs. Ag/AgCl/sat. KCl appears before reaching a steady-state potential of −1.04 V vs. Ag/AgCl/sat. KCl. In contrast, no negative peak of potential is observed and the open circuit potential gradually reaches a steady-state potential of −1.17 V vs. Ag/AgCl/sat. KCl when the duration of the anodic pulse current is less than 40 ms.

SEM observations of the surface of the etched foil show the development of only circular pits before reaching the steady-state potential (Fig. 3a). The circular pits are also found immediately after the sharp potential drop (Fig. 3b). The circular pits are transformed into square pits within 25 ms of dissolution at the steady-state etch potential (Fig. 3c and d). The square pits have a half-cubic shape as observed in a previous study [28]. No pits were observed on the aluminium surface when the duration of the anodic pulse current was 10 ms, in agreement with the fact that the current transient is the same as that in HCl-free H_2SO_4 solution in this period (Fig. 2). A cellular surface texture, found in Fig. 3, is developed during alkaline etching pre-treatment [36].

Fig. 4 shows the change in pit density developed at each anodic pulse interval. The pit densities increase to 2.0×10^6 cm^{-2} up to a pulse time of 40 ms, whereas the pit densities are fairly constant

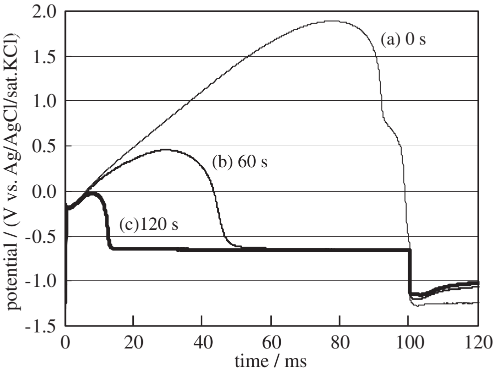

Fig. 1. Chronopotentiograms of aluminium, pre-treated in 1 M NaOH at 60 °C for (a) 0 s, (b) 60 s, and (c) 120 s and subsequently in 1 M HNO_3 solution at 60 °C for 180 s, during anodic pulse current of 100 mA cm^{-2} for 100 ms in a mixed solution of 1 M HCl and 0.1 M H_2SO_4.

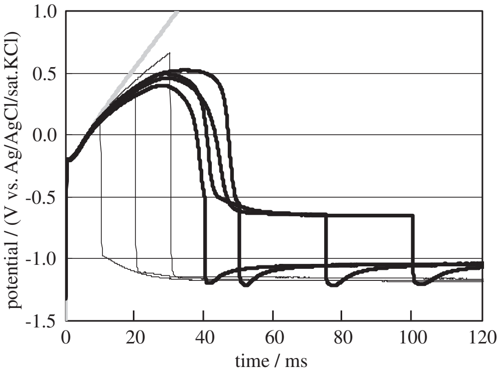

Fig. 2. Chronopotentiograms of aluminium, pre-treated in 1 M NaOH at 60 °C for 60 s and subsequently in 1 M HNO_3 solution at 60 °C for 180 s, during anodic pulse current of 100 mA cm^{-2} for different durations of 10–100 ms in a mixed solution of 1 M HCl and 0.1 M H_2SO_4.