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The growth mechanism of pits in NaCl solution under anodic films on aluminum

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Abstract

Pitting behaviour and pit morphology on anodized pure aluminum in NaCl solution were studied with an electrochemical method and scanning electron microscope (SEM). Severe pitting happened at high potential for anodized pure aluminum. Polarization curves show that the pitting process was diffusion controlled. Many pits with various sizes were observed on sample surfaces after polarization. Some pits developed to several hundreds of microns in diameter, but with the anodic films remaining as covers of the pits. Small openings were seen on the film covers as the diffusion channels for dissolved species within the pits, which reveals that the pits developed in a highly occluded state. The pits show different shapes from hemispherical to oblate. The ratio of pit radius to pit depth, R/t, is proportional to the ratio of pit opening radius to pit radius, r/R. The bigger the ratio r/R is, the more oblate the pit shape is. A modified diffusion controlled model is suggested to explain the formation of oblate pits.

Keywords: Pitting; Anodic film; Aluminum; Pit morphology

1. Introduction

Anodization is extensively used for aluminum and its alloys to increase their corrosion resistance. The anodic film on aluminum is then composed of a compact inner layer and a porous outer layer [1–3]. After sealing process, corrosion resistance of the anodic aluminum film is improved drastically. Corrosion behaviors of anodized aluminum and aluminum alloys have been studied by some authors. Takahashi et al. [4] applied cathodic polarization on aluminum covered with anodic oxide film in neutral borate solution to investigate the produced pits, and found that only the central part of the pits is open to the solution and the periphery is covered with anodic oxide film. Yu and Cao [5] investigated electrochemical behaviour of anodized 2024 aluminum alloy that was sealed with a sealing agent containing Ce. Zuo et al. [6] studied the influence of different sealing methods on pitting resistance of anodized aluminum alloys. Moutarlier et al. [7] investigated the pit morphology of anodized aluminum alloys in detail. It was found that the growing pit developed under the oxide film and a large hemispherical cavity was produced. However, so far the studies on corrosion behaviours of anodized aluminum and aluminum alloys are still not enough. In this paper, pitting behaviour of anodized commercial pure aluminum was studied in order to understand pitting process of anodized aluminum in details.

2. Experimental

The material tested was 99.99% pure aluminum with a thickness of 1.9 mm, in tempered condition. The specimens were mechanically finished with silicon carbide abrasive paper up to 800#, degreased with acetone and rinsed in deionized water. Then the specimens were electropolished in $H_2SO_4+H_3PO_4$ bath at a current density of 200 mA/cm^2 at 70 °C for 5 min. After electropolishing process, the specimens were rinsed thoroughly in deionized water and finally dried in a cold air stream. Anodization was carried out at a constant density of 15 mA/cm^2 in 180 g/l H_2SO_4 bath at 20 °C for 30 min.

Electrochemical measurements were performed in 0.5 M NaCl solution at 25 °C. The solution was prepared from reagent grade chemical and deionized water, and was open

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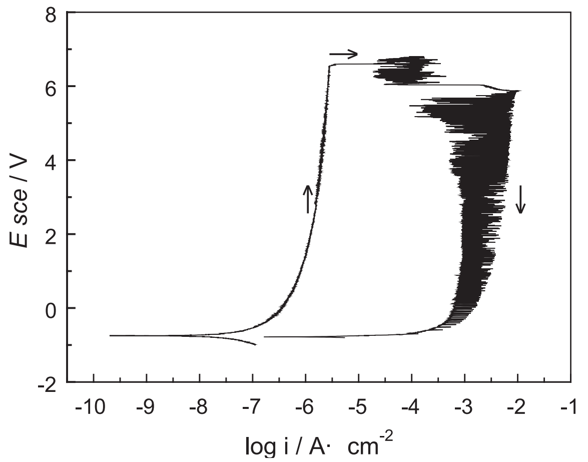

Fig. 1. Potentiodynamic polarization curve of anodized aluminum in 0.5 M NaCl solution.

to the air. The anodized aluminum samples were coated with epoxy resin with an area of 6 mm^2 exposed. The counter electrode was a platinum plate and the reference electrode was a saturated calomel electrode (SCE). Potentiodynamic polarization was carried out at a scanning rate of 1 mV/s, with an EG&G model 273A and M352 corrosion measurement system. After electrochemical experiments, the samples were removed from solution and immediately flushed with deionized water with great care, and dried slowly in a cold air stream. Then the surfaces of the specimens were observed with LEO-1450 scanning electron microscope (SEM).

3. Results

Fig. 1 is a cyclic polarization curve of the anodized aluminum sample in 0.5 M NaCl solution. The anodized aluminum sample showed a stable passivation state and pitting occurred at very high potential. Reverse polarization produced a large hysteresis loop that is a characteristic of pitting corrosion. During the reverse scan, the polarization curve exhibited violent oscillation. This phenomenon may be due to the gas bubbles releasing from the pit mouth during the pit growth. The repassivation potential of the pit is very low, almost equal to corrosion potential, which reflects the characteristic of stable dissolution within the pit.

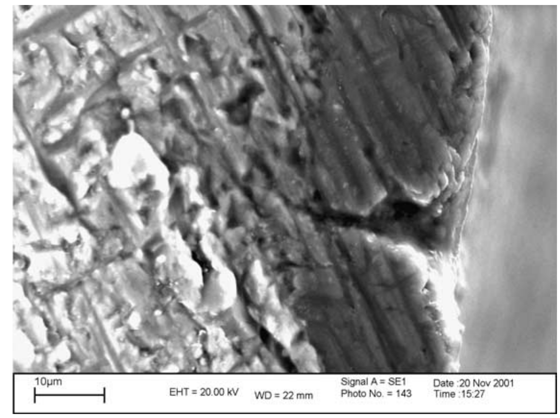

Fig. 3. The cross section of a hole in anodic film.

After polarization test, the anodized aluminum sample surface was observed with SEM. Fig. 2 shows the surface morphology of the anodized aluminum sample after polarization. In Fig. 2a, many small pits with diameters less than 1 µm are seen on the surface. Some of the pits were nucleated around surface inclusions, which may have been introduced during the anodizing process. Fig. 2b shows a pit with a diameter about 6 µm. It seems that the pit did not penetrate the whole thickness of the film, since the thickness of the film is above 10 µm. The pit morphology in Fig. 2a and b suggests that dissolution may have played a role for initiation of pits on the anodized samples, which is possible because the pitting initiating potential is quite high, as shown in Fig. 1. Fig. 3 shows the cross section of an anodized sample on which the film was almost penetrated by a defect. The defect shows an irregular shape, suggesting that the structural imperfections contained in anodic film may play an important role in initiating the breakdown of the film.

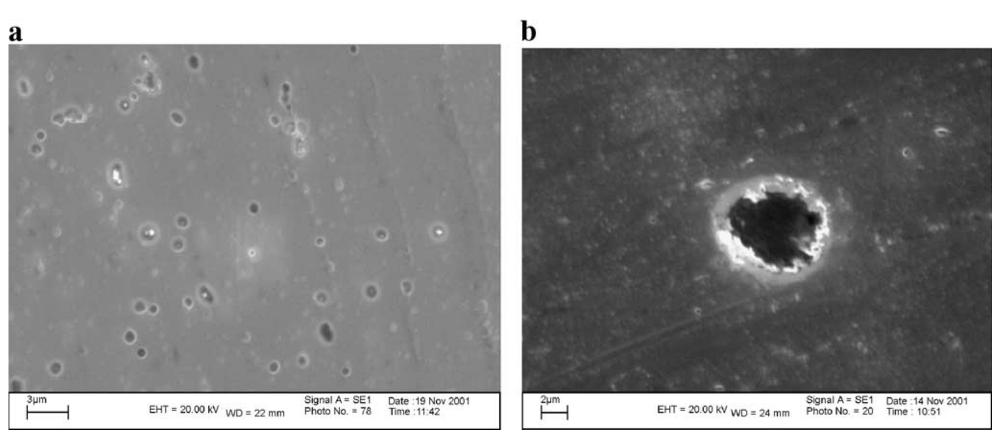

Fig. 2. The morphology of pits on surface of anodic films.