Blister and Pit Formation during Cathodic Polarization of Aluminum Covered with Anodic Oxide Films -In-situ AFM Observation-

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Introduction

One of the authors has investigated the cathodic polarization of aluminum covered with anodic oxide films in neutral solutions [1 – 4]. It was found in the previous studies that many pits are formed on the aluminum substrate during cathodic polarization, and that the number and size of pits strongly depend on pH-buffer action of solutions and the surface pretreatment of specimens. The pit formation is considered to be due to local alkalization at the interface between anodic oxide films / the metal substrate. The following reactions may occur at the interface during cathodic polarization.

$$H^+ + 2e^- = H_2 \quad (1)$$

$$2H_20 + 2e^- = H_2 + 2OH^- \quad (2)$$

$$Al + 3H_2O + OH^- = Al(OH)_4^- + (3/2)H_2 \quad (3)$$

The initiation of the pit formation, however, remains unknown on the transport of H^+ or H_2O across the oxide film to the interface between anodic oxide films / the metal substrate.

In the present investigation, the initial stage of cathodic polarization of aluminum covered with barrier type anodic oxide films has been examined in a neutral borate solution by in-situ atomic force microscopy (AFM).

Experimental

1) Specimen: Highly pure aluminum foil (99.99 mass%) was cut into 1 x 2 cm and electropolished in a perchloric acid / acetic acid solution. The electropolished specimen (Specimen-I) was anodized in 0.5 kmol m^{-3}-H_3BO_3 / 0.05 kmol m^{-3}-$Na_2B_4O_7$ solution at 293 K to form barrier type oxide films. Anodizing was carried out by applying a constant c. d. of 10 A m^{-2} up to E_a = 5 and 50 V (Specimen-II, -III) .

2) Cathodic polarization and in-situ AFM: Specimen-I, -II, and -III were set in an electrochemical cell on the AFM stage, and then cathodically polarized with a constant current of i_c = 5 and 500 A m^{-2} for 10 – 2500 s in 0.5 kmol m^{-3}-H_3BO_3 / 0.05 kmol m^{-3}-$Na_2B_4O_7$ solution. During cathodic polarization, the time-variation in the specimen potential (vs. Pt wire) was measured, and the surface morphological change was observed by in-situ AFM with a silicon probe.

3) Characterization: Scanning laser confocal microscopy (SLCM) and field emission scanning electron microscopy (FESEM) were used for the characterization of the specimen surface.

Results and Discussion

Figure 1 shows in-situ AFM three-dimension (top) and height (bottom) images of Specimen-II cathodically polarized at i_c = 500 A m^{-2} for a) t_c = 10, b) 300, c) 600, and d) 900 s. All the figures were obtained at the same area of specimen at 25 x 25 μm. A blister can be observed on the surface at t_c = 10 s (Fig. 1-a), and this is due to the hydrogen evolution at the interface between anodic oxide film and the metal substrate in the blister. The top part of the blister becomes concave at t_c = 10 s (Fig. 1-b), due to the hydrogen release from the blister through oxide film imperfections. After the film is removed at the blister position, the metal substrate dissolves at the bottom of blister (Fig. 1-c), eventually leading to pit formation at the center of the film removed area (Fig. 1-d).

Blister and pit formation was also observed for Specimen-III, but only pit formation was observed for Specimen-1during cathodic polarization.

References

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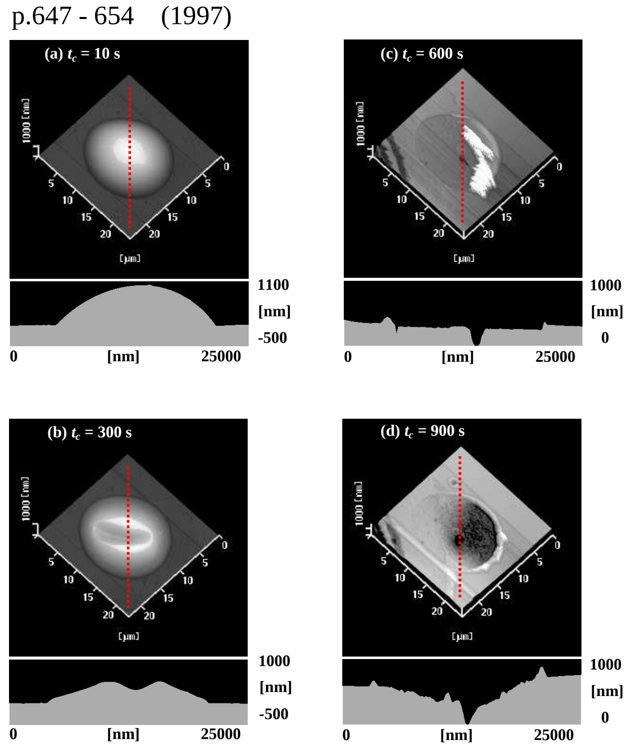

Fig. 1. In-situ AFM three-dimension (top) and height (bottom) images of Specimen-II cathodically polarized at i_c = 500 A m^{-2} for a) 10, b) 300, c) 600, and d) 900 s in 0.5M-H3BO3 / 0.05M-$Na_2B_4O_7$