

Effect of Mechanical, Chemical, and Thermal Treatments on the Repairing of Voids in the Re-Anodizing of Composite Oxide Films on Aluminum

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Introduction

Composite oxide films formed on aluminum by anodizing after hydrothermal treatment is used as a dielectric layer in aluminum electrolytic capacitors, and generally consist of two layers: an outer γ - Al_2O_3 -containing layer and an inner amorphous Al_2O_3 layer¹. In the outer layer there are lots of voids linked with each other through fine cracks, forming a network structure. Some of voids could be isolated from others².

The voids are filled with oxides by relaxation and re-anodizing industrially to extend the service life of the electrolytic capacitor. Treatments for linking the isolated voids are necessary to fill the voids effectively through relaxation and re-anodizing.

In this investigation, mechanical, thermal, and chemical treatments were carried out before relaxation and re-anodizing to examine how these treatments influence the void-repairing in the subsequent re-anodizing.

Experimental

i) Specimen: Highly pure aluminum foil (99.99%) was used as specimens after electropolishing in a perchloric acid / acetic acid mixture.

ii) Hydrothermal treatment and anodizing: The specimens were immersed in boiling pure water for 30 min and then anodized in 0.5 M- H_3BO_3 / 0.05 M- $\text{Na}_2\text{B}_4\text{O}_7$ at 333 K with a constant current of 10 Am^{-2} to 300 V (vs. Ag/AgCl).

iii) Thermal, mechanical, and chemical treatments: The anodized specimens were heated in air at 773 K for $t_h = 0.5\sim 72$ h as heat treatments. As mechanical and chemical treatments, the anodized specimens were immersed in 50 wt%- H_3PO_4 at 293 K with / without ultra sonic wave at 34 kHz and 50 W for $t_c = 15\sim 60$ min. Combinations of thermal and chemical treatments were also carried out.

iv) Relaxation and re-anodizing: The specimens with thermal, mechanical, and chemical treatments were immersed in the boric acid / borate solution at 333 K for 10 min and then re-anodized in the same solution with $i_r = 1 \text{ Am}^{-2}$. The change in the anode potential, E_r , with re-anodizing time, t_r , was monitored with a digital multimeter connected to PC system. The E_r was set so as to be kept at 300 V, when it reach the value.

Results and discussion

Figure 1 shows the E_r vs. t_r curves for specimens with thermal treatments for $t_h = 0\sim 72$ h. The $t_h = 0$ in Fig. 1 means no heat treatment. The $t_h = 0$ specimen shows a 30 V-jump in E_r at the very initial stage and then a stepwise increase in E_r with t_r , indicating a flat slope region between 170 and 220 V before the curve becomes steeper up to $E_r = 300$ V. The relatively complicated behavior is due to a distribution of void concentration across the anodic oxide films.

The heat-treated specimens show no E_r -jump at the

initial stage and no rapid increase in E_r at the final stage of re-anodizing. The time necessary for E_r to reach 300 V increases with increasing t_h . These behavior can be explained by the development of network structure of voids due to crystallization of oxide during heat treatments.

Figure 2 shows the E_r vs. t_r curves for specimens with chemical treatments in H_3PO_4 solution for $t_c = 0\sim 60$ min. The time necessary for E_r to reach 300 V increases considerably with increasing t_c , and this is due to the enlargement of crack diameter by dissolution of oxide during chemical treatment.

Application of ultra sonic wave in H_3PO_4 for more than 30 min influenced the E_r vs. t_r curve. Thermal treatment followed by chemical treatment showed a synergistic effect on void-repairing in re-anodizing, while the opposite order of the treatments showed no effect.

References

- 1) H. Takahashi, Y. Umehara, T. Miyamoto, N. Fujimoto, and M. Nagayama, *J. Metal Fin. Soc. Jpn.*, **38**, 67 (1987)
- 2) T. Kudo, R. S. Alwitt, *Electrochim. Acta*, **23**, 341 (1978)

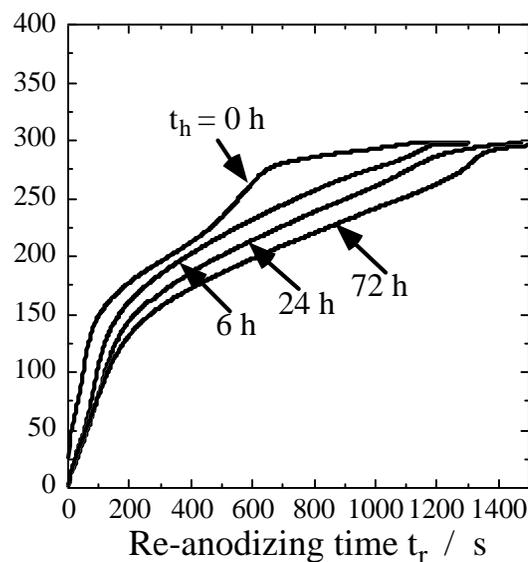


Fig. 1 Change in anode potential, E_r , with re-anodizing time, t_r , for specimens with heat treatments for different periods.

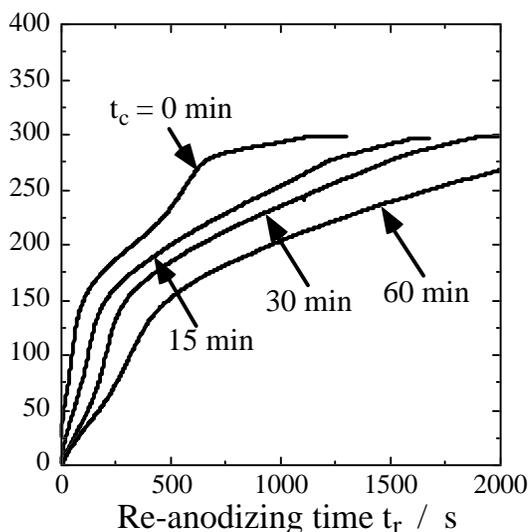


Fig. 2 Change in anode potential, E_r , with re-anodizing time, t_r , for specimens immersed in H_3PO_4 solution for different periods.