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CRYSTAL TRANSITION PROCESS DURING POST-BREAKDOWN IN THE MOLTEN SALT

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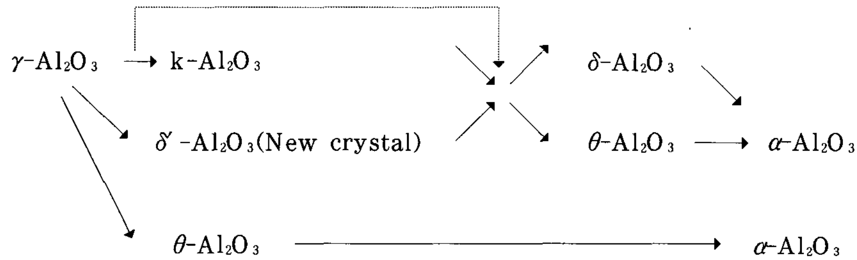
Abstract

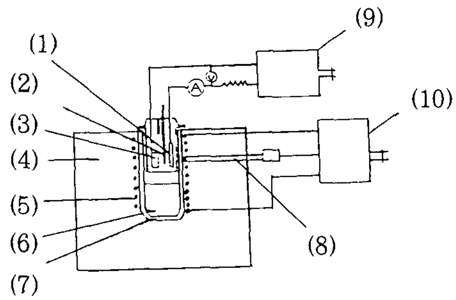
The morphology and composition of anodic films, formed on aluminium at various current densities, in the range 1-100 Am^{-2}, in the molten bisulphate melt at different temperatures(418-498K), have been studied using transmission electron microscopy of ultramicrotomed film sections, and ion beam thinned films. From the structural analysis of the electron diffraction patterns taken from the ultramicrotomed sections and ion beam thinned films, it can be concluded that the crystal modification process from γ-Al_2O_3 to α-Al_2O_3 proceeds in the following steps :



Key words : *Anodic oxidation, Post breakdown, Molten salt, Crystal transition, Aluminum*

1. INTRODUCTION

Electrical breakdown during anodizing of aluminum has been the subject of intensive investigation, because of its practical importance in operating electrolytic capacitors. Tajima et. al[3] showed that anodic films formed in molten bisulphate melts developed α-alumina [1] with small proportion of γ-alumina[2] during electrical breakdown[4)-6)]. The α-alumina formation mechanism is not yet fully understood, although the process was developed by Tajima et. al[3] in 1959. Little



(1) specimen
(2) mercury-in-glass thermometer
(3) platimium cathode (4) cylinder furnace
(5) heating element (6) insulator
(7) cylindrical alumina tube
(8) thermocouple (9) power supply
(10) autom. temp. controller

Fig. 1 Schematic diagram of the experimental set-up for anodizing in molten salt

fundamental work is evident in the literature which comprises generally of several technical investigations which are concerned mainly with the commercial production of a ruby film.

In the present research, direct transmission electron microscopy of the stripped films, ion beam thinned films and occasional ultramicrotomed film sections were employed to gain further insight into the mechanism of the electrical breakdown during anodizing of aluminum in the molten salt.

2. EXPERIMENTAL RESULTS

The morphology and composition of anodic films, formed on aluminium at various current densities, in the range 1-100 Am^{-2}, in the molten bisulphate melt at different temperatures (418-498K), have been studied using transmission electron microscopy of ultramicrotomed film sections, and ion beam thinned films. When electro-

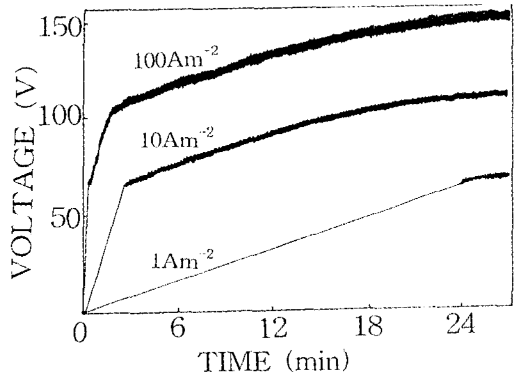
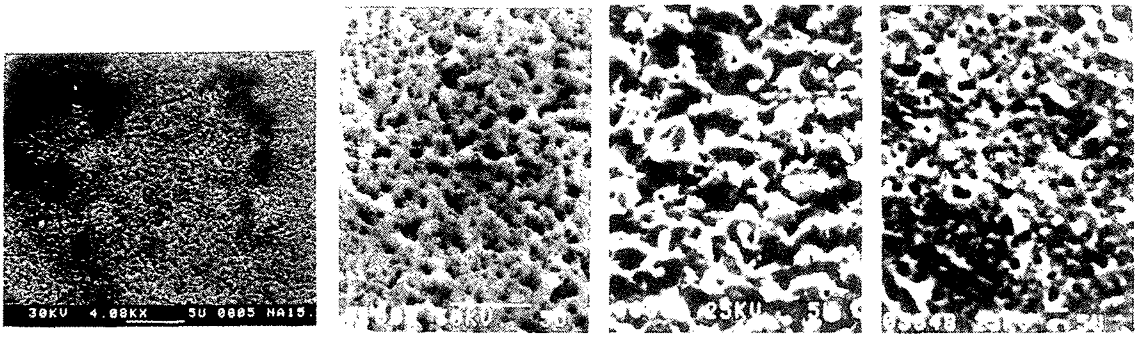


Fig. 2 Voltage/time behaviour for anodizing pure aluminum at various constant current densities in molten salts at 458°K

polished aluminium is oxidized anodically in the molten salt, the current density, I, through the anodic films shows a marked exponential dependence on the field, E, across the film. Furthermore, the dependence of the field strength on ln i at different temperatures, i. e. the Tafel slope, dE/d ln i,was found to be approximately constant with increase of temperature.

The anodic films formed in the molten salt are generally barrier type and the current efficiency for film growth is approximately 100% until electrical breakdown occurs. The morphology and composition of the films formed on aluminium during post-breakdown in the molten salt have been studied by RBS and transmission electron microscopy of ultramicrotomed film sections and ion beam thinned films. On detailed examination of the anodic films, formed at 10 Am^{-2} in the molten salt, after breakdown for various times in the range 30 sec~20min., two distinct phases were revealed ; i. e. amorphous and crystalline alumina. It is interesting that the breakdown region at the center of the crater has an amorphous

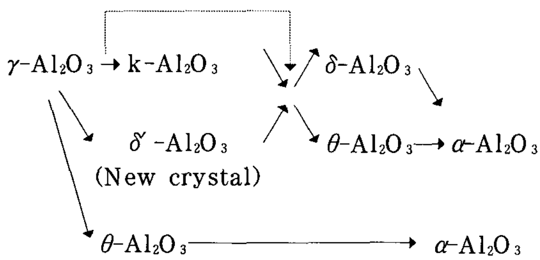


(a) (b) (c) (d)

Fig. 3 Scanning electron micrographs of the surface morpholo-gies of the films formed at 100 Am^{-2} after breakdown for various times in the molten salt at 498K.
(a) 30 second breakdown, Magnificatio, 4080 (b) 1 minute breakdown, Magnificatio, 3600
(c) 5 minute breakdown, Magnificatio, 9000 (d) 20 minute breakdown, Magnificatio, 9000

sulphur-containing film material, with a well-developed scalloped region in the substrate. This indicates that when an appreciable voltage drop occurs across the thin film region after sparking, the quenching effect by the rapid discharge process occurs. Then, the bottom of the pit-like region may be rehealed at high effective current density and relatively low temperature. This explains the presence of sulphur within the film after breakdown for 5 min.

From the structural analysis of the electron diffraction patterns taken from the ultramicrotomed sections and ion beam thinned films, it can be concluded that the crystal modification process from γ-Al_2O_3 to α-Al_2O_3 proceeds in the following steps :



Therefore, the direct crystal modification from γ-Al_2O_3 to α-Al_2O_3 does not occur. Furthermore, the electron diffraction patterns of the intermediate modifications, such as κ-Al_2O_3, ζ-Al_2O_3 and θ-Al_2O_3 in γ-Al_2O_3 matrix have strong (440) and (400) reflections of γ-Al_2O_3, indicating that the transition process is responsible for the rearrangement of cations in γ-Al_2O_3 matrix. In addition, it was found in this research study that a new crystalline modification of alumina, δ'-Al_2O_3, has a tetragonal unit cell of lattice parameters, a =1.240nm and c=0.991nm, respectively.

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