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ELECTRICAL BREAKDOWN INITIATION OF ANODIC FILMS DURING ANODIZING IN MOLTEN BISULPHATE MELT

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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. The first sign of incipient breakdown revealed by transmission electron microscopy of stripped films, is always the appearance of dark regions about 1,000 nm in diameter, representing local overgrowth of the film. The breakdown mechanism is closely related to thermal effects, because temperature rises at regions representing local overgrowth in the stripped films were observed at voltages close to the breakdown voltage, likely arising through impact ionization.

Key words : *Anodizing, Breakdown initiation, Molten salt, Electrical breakdown, 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[1, 2] The understanding of the mechanism of the electrical breakdown is also of fundamental importance for anodizing in general, since the onset of breakdown terminates the normal film growth process over the macroscopic metal surface. Several mechanisms have been proposed to explain the breakdown, such as electronic impact ionization and avalanching[1, 2, 3, 6], local heating due to the conduction through electrolyte-filled microfissures in the anodic film[4], and local crystallization in the amorphous anodic film[5, 6]. In the present research, high resolution scanning electron microscopy of the anodized surfaces and 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 initiation 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. Anodizing of aluminium at constant current density in molten, eutectic bisulphate melts results in the development of amorphous anodic alumina, which has been examined by transmission electron microscopy with EDX facilities and other analytical procedures. Over a wide range of anodizing conditions, barrier type anodic films are developed at high current efficiency at voltages below the dielectric breakdown voltage.

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When impact ionization occurs at the low activation energy region of the aluminium substrate, i. e. grain boundary of substrate, then, motion of excessive activated positive ions (aluminium ion) from the substrate towards the film /electrolyte interface increases the resultant field strength across the film. This field enhancement process generates further electronic current at the film/electrolyte interface and increases the temperature in the film.

From the observation of γ-Al_2O_3 in the inner relatively pure alumina region, development of crystalline γ-Al_2O_3 in amorphous alumina is thought to be related to local heating effects, associated with the electronic conduction process through the filament in the anodic film occurring at the low activation energy sites on the aluminium substrate above the critical film thickness of certain field strength.

The outer sulphate incorporated layer of the film in the vicinity of the conducting channels, where the temperature is above 1,200 K, is no longer stable and decomposes to SO_2 gas, which may produce further conducting channels. This manner of conducting channel multiplication may eventually cause the channel, surrounded by a band of thick film material.

After this stage, more serious discharge of the specimen's stored energy is thought to occur, accompanied by sparking, through the relatively extensive conducting channel, causing local evaporation of the decomposed incorporated ions from film material and structural change process due to high temperature and high ionic movement.

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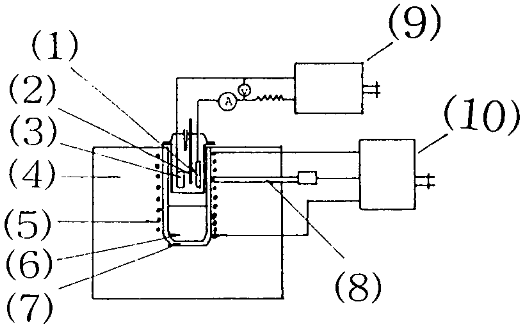

(1) specimen
(2) mercury-in-glass thermometer
(3) platinium cathode
(4) cylinder furnace
(5) heating element
(6) insulator
(7) cylimdrical alumina tube
(8) thermocouple
(9) power supply
(10) autom. temp. controller

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

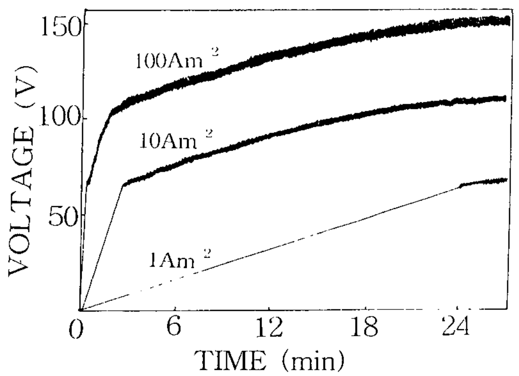

Fig. 2 Voltage/time behaviour for anodizing pure aluminum at various constant current densities

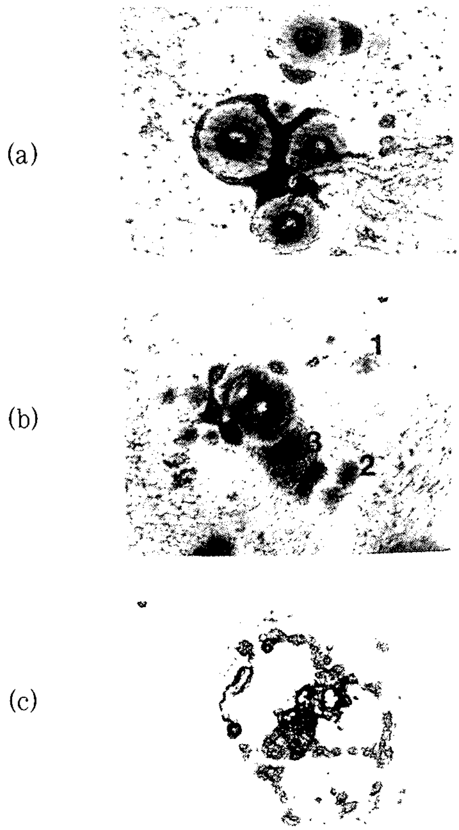

Fig. 3 Transmission electron micrographs of the stripped films formed at 10 Am^{-2} to various voltages in the molten salt at 418 K
(a) 65V, Magnification, 5900
(b) 65V, Magnification, 7500
(c) 65V, Magnification, 5900