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SHORT COMMUNICATION

The Use of the 1 MeV Electron Microscope to Study Anodic Oxide Films formed in the Tunnels of Etched Aluminium Foil

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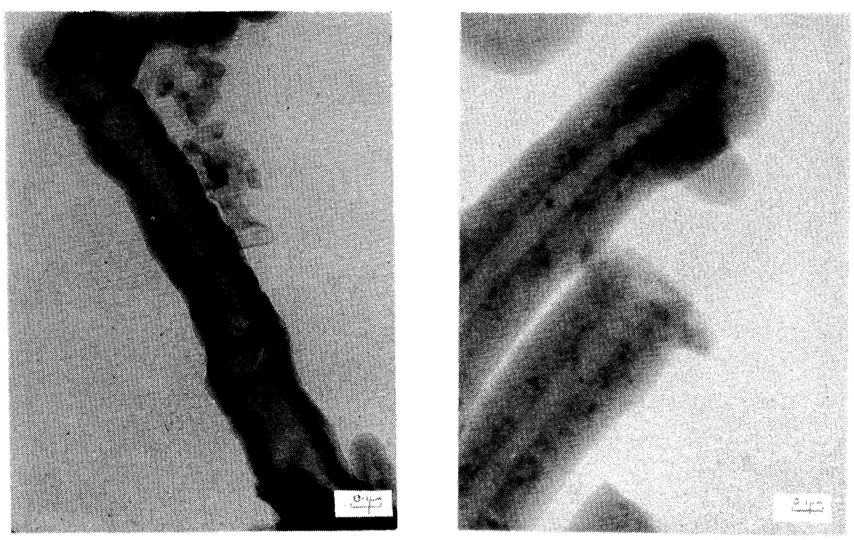
Transmission electron microscopy of thin anodic oxide replicas has been employed for studying the surface morphology of etched aluminium foil[1], a material widely used for the preparation of aluminium electrolytic capacitors. More recently the tunnel structure produced by the etching process below the surface has been studied by examining the oxide replicas in the scanning electron microscope[2–5]. The advent of the 1 MeV electron microscope with its improved penetrating power permits much thicker oxide films to be examined directly in transmission. This technique has now been used to study the anodic oxide layers formed within the tunnel network. Such information is particularly important in relation to higher anodising voltages, where problems may arise in forming good dielectric layers near the bottom of the tunnels.

For this work standard high gain foil, having tunnel widths in the range 0.1–0.3 μm was anodised at constant voltage in either phosphoric acid-borax or phosphoric acid-ammonium pentaborate electrolytes for periods of 5, 15 or 30 minutes. The oxide was separated from the metal by treatment in Br_2-methanol and then examined in the microscope. Examples of the appearance of the oxide layers in the tunnels are shown in Figure 1. A study at three anodising voltages of 25, 75 and 125 V indicated that the oxide films were of uniform thickness along the length of the tunnels for a given set of anodising conditions and that the width of the tunnels de-

(a)
x40000



(b)
x40000

FIGURE 1 Transmission micrographs of oxide films formed in the tunnels of etched aluminium foil anodised in H_3PO_4-borax electrolyte (pH = 5.5) at 98°C for 30 minutes: (a) 25 V, (b) 125 V.

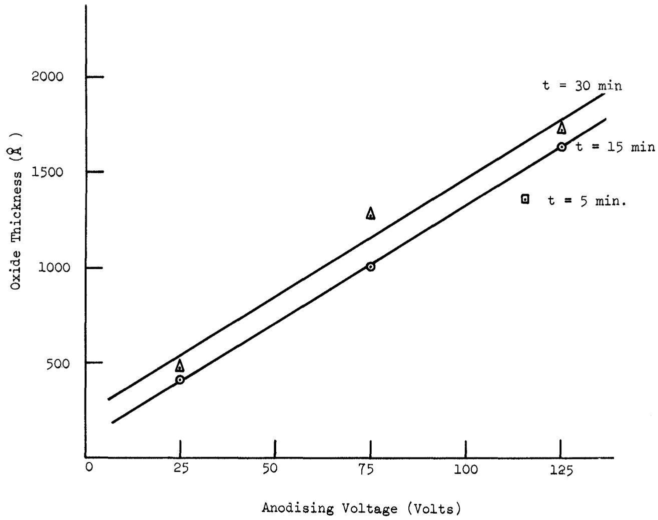


FIGURE 2 Variation of oxide thickness with voltage and time of anodising. Anodising electrolyte: H_3PO_4-borax (pH = 5.5), temperature = 98°C.

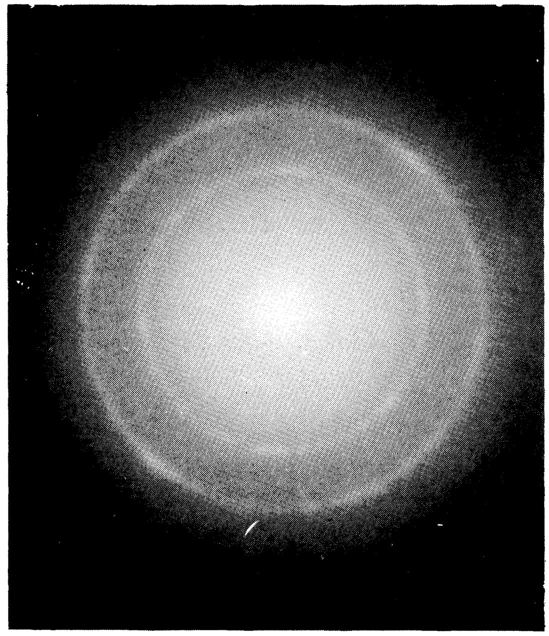
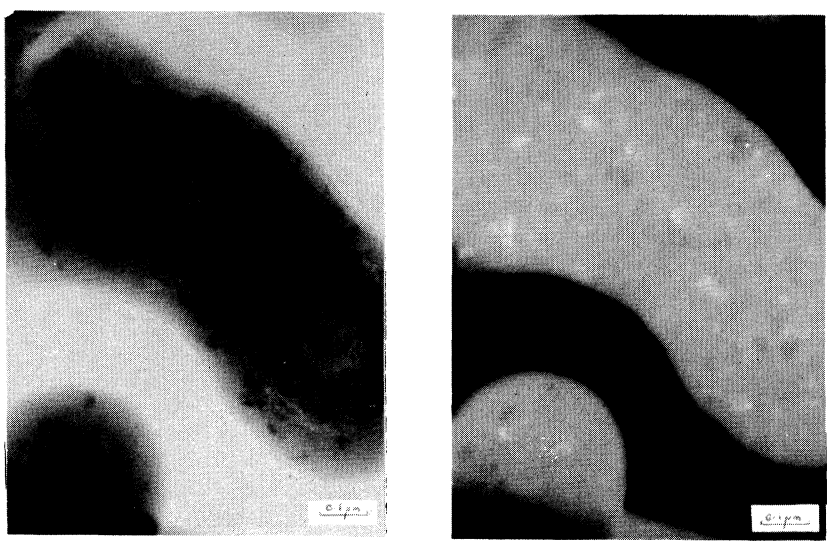


FIGURE 3 Electron diffraction pattern from a specimen formed at 125 V in H_3PO_4–$NH_4B_5O_8$ (pH = 5.5) at 98°C for 30 minutes.

creased with increasing voltage. The relationship between oxide thickness and voltage for different anodising times is shown in Figure 2. The average thicknesses per volt are 10.9 Å (one result), 13.4 Å and 14.8 Å for 5, 15 and 30 minutes anodisation times respectively.

Dark spots were apparent in the films, particularly those formed at 75 V and 125 V. These were investigated in the microscope using diffraction (Figure 3) and dark field (Figure 4) techniques. Whereas the bulk of the layers was found to be amorphous, the dark spots were shown to be γ'-alumina having a crystallite size in the region of approximately 100 Å. The slightly diffuse character of the rings shown in Figure 3 is caused by the presence of large amounts of amorphous oxide in the background.

(a) x63000



(b) x63000

FIGURE 4 Transmission micrography from a specimen formed at 125 V in H_3PO_4–$NH_4B_5O_8$ (pH = 5.5) at 98°C for 30 minutes: (a) Bright field, (b) dark field.

In the light of these preliminary studies it is believed that the high voltage electron microscope will be a useful tool for studying anodic oxide and other thin films.

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