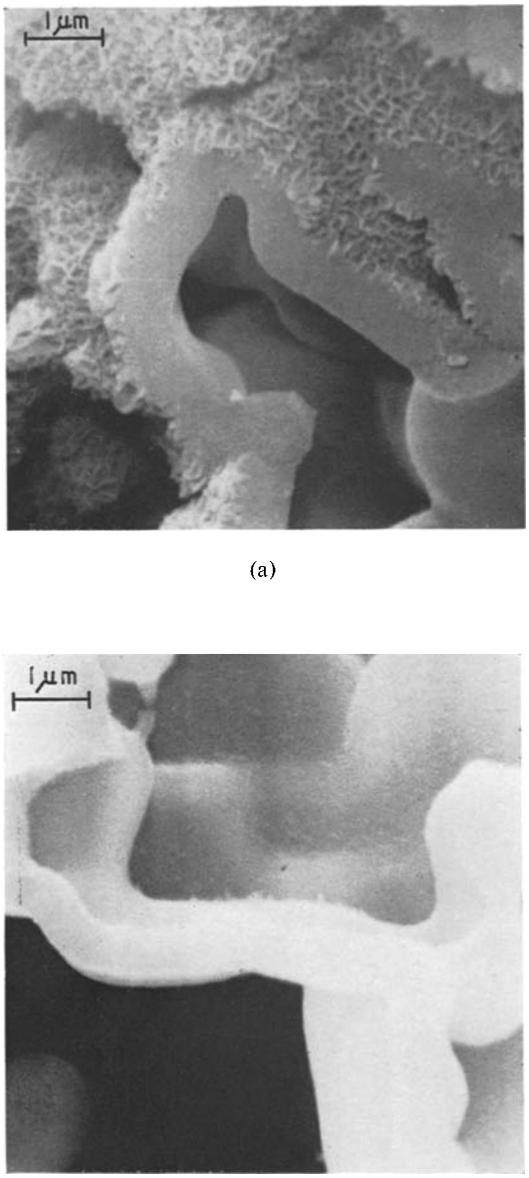

(a)

(b)

Plate. 1. Sections of isolated dielectric oxides formed on etched aluminium foil after hydration and subsequent anodization at 650V. (a) As anodized. (b) After thinning with acid reagent.

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TECHNICAL NOTE

The structure of anodic oxide films formed on pre-hydrated Al

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In the manufacture of high voltage aluminium electrolytic capacitors, it is the usual practice to immerse the etched anode foil in boiling water for several minutes prior to anodizing. This treatment, which deposits a layer of hydrated aluminium oxide at the metal surface, results in a substantial saving of electricity during the subsequent anodization. Other workers [1] have established that the surface layer produced by the hydration process is pseudo-boehmite, a form of boehmite containing excess hydroxyl groups. It is the purpose of this note to show that the boehmite is retained at the outer surface of the dielectric oxide after anodization.

Samples of either etched or plain aluminium foil were immersed in boiling, deionized water for 4 min. and then anodized at 650 V in hot boric acid for 20 min. The scanning electron micrograph of Plate. 1(a) shows a section of the oxide from the etched foil, separated from the metal by dissolution of the metal in bromine-methanol solution. The upper surface (oxide-electrolyte interface) is covered with a network of ridges or platelets corresponding closely to the description of pseudo-boehmite given by Vedder and Vermilyea [1]. In contrast, the under surface (oxide-metal interface) is essentially smooth. When the anodized foil was treated with a chromic oxide-phosphoric acid solution at 90°C for 5 min. the hydrated outer layer was dissolved (Plate 1(b)). X-ray analysis of the stripped oxides indicated the presence of both boehmite and a γ-type alumina, only the latter being present after the acid treatment. The crystallite size of the boehmite was in the region of 180 Å and that of the alumina 260 Å, both values having an order of accuracy ± 50%.

Similar topographies were observed with the plain foil. Glancing angle electron diffraction confirmed the presence of boehmite at the oxide-air interface, both on the hydrated and, also, on the hydrated and anodized film. Transmission electron microscopy (carbon replication) of the oxide-air interface after the acid treatment, indicated a smooth surface intersected by a number of thinner regions which had been attacked by the acid. Selected area electron diffraction established that the bulk of this residual layer was γ'-alumina of crystallite size 200 Å (±30Å), and that the regions where thinning had occurred corresponded to an amorphous phase.

To summarize, the structure of the anodized dielectric produced on hydrated aluminium foil has been found to consist of an upper layer of boehmite having a comparatively open structure. Underneath this is a dense film of essentially uniform thickness, consisting largely of γ'-alumina together with a small amount of amorphous material, presumably also alumina. It is concluded that the anodic oxide is formed below the layer of boehmite deposited by the hydration process.

References

[1] W. Vedder and D. A. Vermilyea, *Trans. Faraday Soc.*, **65** (1969) 561.