

based on that of  $\beta$ -FeOOH and since the letter  $\beta$  has not been assigned to any other modification we propose to call it the  $\beta$ -form.

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<sup>1</sup> Gallagher, K. J., *Nature*, **226**, 1225 (1970).

## Branching Colony Pore Structure in Anodic Alumina Films

A LARGE cellular structure may be present underneath thick porous anodized films grown on aluminium in chromic acid and an alkaline borate electrolyte<sup>1</sup>. We termed these "secondary" cells because their population was much smaller than the number of pores in the anodic film as counted from electron micrographs of either surface replicas of thick films or transmission through very thin ones. It appears that these cells are not related to the pretreatment or subgrain structure of the base metal. Their presence has now been confirmed by electron-optical examination of cross-sections of anodic films grown on super-pure aluminium (99.999%) in a 10% chromic acid solution at 30 V, 40° C. The method for the preparation and taking replicas of film sections was similar to that described by Wood and O'Sullivan<sup>2</sup>. An A.E.I. 'E.M.6.G.' electron microscope was used for the examination of the replicas.

A major feature of the cross-section is branching of the pores to form a colony structure. As film growth continues into the metal, the pores branch, resulting in a curved growth front for the colony (the metal being oxidized most rapidly parallel to the pore axis). Where two colonies adjoin, pores become inactive; this leads to the cessation of some and

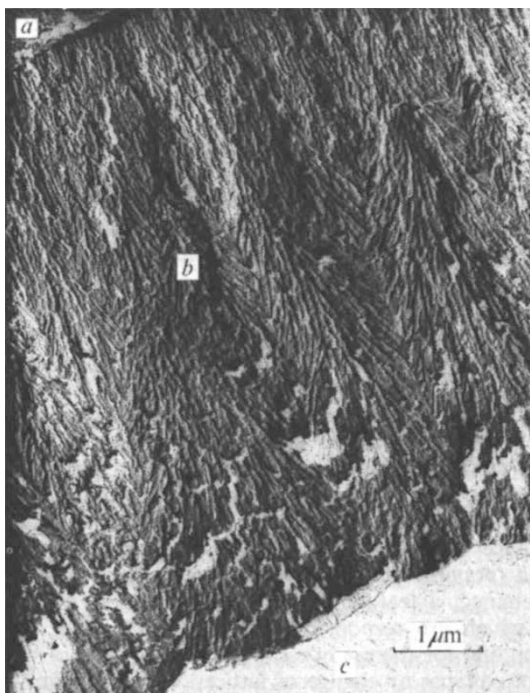


Fig. 1 Cross-section of anodic oxide film grown in a 10% chromic acid solution at 30 V, 40° C. Au-Pd shadowed carbon replica. a, Oxide surface; b, "pored" oxide; c, metal substrate.

simultaneous creation of other pore channels. The total population of the pores remains unchanged and the number of the "primary" cells, those associated with pores, is identical to that of the pores counted on film surface<sup>1</sup>. "Secondary" cells are formed by the curved growth fronts.

Branching of pores and the "secondary" cells are not typical features of the "ideal" anodic film structure as reported by Keller *et al.*<sup>3</sup>, and confirmed by many workers for oxalic<sup>2</sup>, phosphoric<sup>4</sup> and sulphuric<sup>5</sup> acids. The barrier film, too, is less well defined in the micrograph shown (Fig. 1), although the occasional growth cell can be detected with a central pore terminating just short of the metal-oxide interface.

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<sup>1</sup> Neufeld, P., and Ali, H. O., *Trans. Inst. Met. Finish.*, **48**, 175 (1970).

<sup>2</sup> Wood, G. C., and O'Sullivan, J. P., *J. Electrochem. Soc.*, **116**, 1351 (1969).

<sup>3</sup> Keller, F., Hunter, M. S., and Robinson, D. L., *J. Electrochem. Soc.*, **100**, 411 (1953).

<sup>4</sup> O'Sullivan, J. P., and Wood, G. C., *Proc. Roy. Soc. (Lond.)*, **317**, 511 (1970).

<sup>5</sup> Booker, C. J. L., Wood, J. L., and Walsh, A., *Nature*, **176**, 222 (1955).

## Dehydroxylation of Anatase Surface by Irradiation and Nature of Adsorbed Water

INFRARED<sup>1-3</sup>, chemical<sup>4-6</sup> and other physical measurements<sup>7-13</sup> on titanium dioxide have shown the presence of surface hydroxyl groups which are progressively removed above 200° C. We have studied the adsorption of water on anatase and preliminary analysis of the data shows that ultraviolet irradiation also causes dehydroxylation of the surface and that water is possibly chemisorbed at the vacant sites of hydroxyl groups at room temperature. Photodehydroxylation may play a very significant role in imaging processes<sup>14,15</sup> and in oxidation-reduction reactions<sup>16,17</sup> on the semiconductor surface.

Titanium dioxide, made by flame hydrolysis of  $\text{TiCl}_4$ , was in the form of randomly oriented anatase. All metallic impurities were less than 5 p.p.m. Conductivity grade distilled water was freed from dissolved gases by alternately freezing and melting under vacuum. The adsorbent samples were confined in a quartz bulb and adsorption measurements were made in a conventional volumetric system using a mercury monometer. A mercury lamp, 'G.E. H-100A-4T', was used for irradiation.

Adsorption isotherms are shown in Fig. 1. To eliminate the effect of extraneous gases and vapours the titanium dioxide samples were outgassed at 150° C and then equilibrated with water vapour before each experimental run. Six identical adsorption isotherms (curve A) were obtained at 0° and 22° C on samples outgassed at 22°, 70° and 150° C and the curve is entirely reversible. The isotherms (curve B) determined for irradiated samples almost exactly overlap the isotherms for samples outgassed at 550° C. At 550° C titanium dioxide surface becomes completely dehydroxylated<sup>18</sup>; thus the overlap of isotherms demonstrates that irradiation may also cause dehydroxylation. Curve B is reversible only down to its first "knee" corresponding to a relative pressure of  $\sim 0.1$ .

When the anatase sample, outgassed thermally at 150° C or by irradiation, is exposed to water vapour under reduced pressure at room temperature, the adsorption isotherm overlaps curve A of Fig. 1. If the evacuation is carried out at