TABLE I Comparison of the gradients of the linear least squares fits for fracture strength and Young's modulus against fibre diameter for fibres heat treated to 1000 to 1200 °C, 1500 °C and 2500 °C

| Final heat treatment temperature of fibres, ° C | Gradient of fracture strength versus fibre diameter $GNm^{-2}/\mu m$ | Gradient of Young's modulus versus fibre diameter $GNm^{-2}/\mu m$ |
|---|---|---|
| 1000 to 1200 | 0.09 | 7.6 |
| 1500 | 0.29* | 21.0* |
| 2500 | 0.55 | 45.0 |

*Values calculated from reference 2.

graphite crystallites which form on subsequent heat treatment [5]. In most commercially available PAN precursor fibres, the preoxidation treatment is discontinued before complete oxidation of the precursor is achieved so that a "core" of unoxidised, unstabilised PAN remains. This results, after further heat treatment, in a duplex fibre structure with an outer "sheath" of well aligned crystallites and an inner "core" of less well aligned crystallites. As the final HTT is increased the alignment of the basal planes of the crystallites parallel to the fibre axis also increases. Thus, since the Young's modulus of the fibre is extremely dependent on the orientation of the crystallites, the "sheath" will have a higher Young's modulus than the "core". The diameter effect can then be explained in terms of the "law of mixtures" since the proportion of "core" in the thick fibres will be greater than in thin fibres. Increasing the final HTT will accentuate the difference between the Young's moduli of the "sheath" and "core" structures so that the increasing dependence of Young's modulus on fibre diameter is to be expected.

The dependence of fracture strength on fibre diameter can also be explained in terms of the sheath/core structure. On cooling from the final HTT, flaws will be formed due to internal stresses resulting from the differential thermal contraction in adjacent crystallites. The number of flaws formed will be greater in the less well aligned "core" region, but will also increase with the higher HTT due to increased internal stresses. In addition, because of the improvement in structure of the "sheath" with higher HTT, fewer flaws would be expected in this region of the fibre and hence the *difference* in the number of flaws occurring in the "sheath" and "core" will increase with HTT. The dependence of fracture strength, which is related to the flaws present, on fibre diameter is therefore expected to increase with increasing HTT.

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## *The Microstructure of Plasma-Anodised Alumina Films*

Plasma anodising has been used by several workers [1-10] as a means of growing oxide layers on metals and semiconductors, and it is now finding application in the manufacture of electronic devices [11]. Surprisingly little attention has been paid to the microstructural aspects of the resulting oxide, and the purpose of this letter is to point out the potentialities of scanning electron microscopy for revealing the microstructure, and to indicate an important problem which can be studied by this means.

A piece of aluminium sheet 10 mm square by 1 mm thick was polished mechanically to produce a flat surface, and then polished electrolytically in a perchloric-acetic acid mixture to remove the cold-worked layer. Part of the surface was masked with lacquer, so as to provide a reference surface without an anodised film. The specimen was then transferred to a conventional vacuum-evaporator pumped by a liquid-nitrogen-trapped oil diffusion pump. After

pumping down, oxygen of commercial purity was admitted continuously into the bell-jar via a drying trap and a needle valve to a pressure of 30 to 50 mtorr and pumped out continuously by the partially-baffled diffusion pump. A direct-current plasma was generated between aluminium disc electrodes at a current of 10 mA, following the method of Lee *et al* [10]. The specimen was inserted into the plasma near the cathode, but facing away from the cathode to avoid picking up sputtered cathode material [10]. A constant current of 2 mA was drawn for 3 h, so that during the oxidation the potential of the specimen varied with respect to the plasma. The specimen was removed and the lacquer was dissolved with acetone. A distinct interface was visible between the formerly lacquered and unlacquered parts.

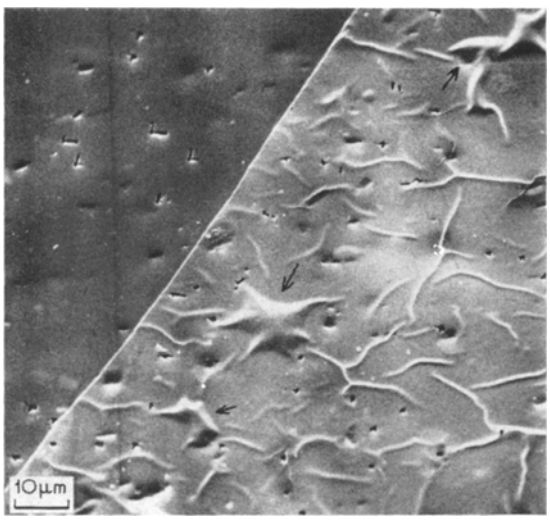


*Figure 1* Interface between oxidised and reference surfaces (oxide in lower right part of micrograph).

A portion of the specimen was examined in a Stereoscan microscope. Charging of the oxidised surface occurred, and it was therefore necessary to deposit a gold conducting layer. Micrographs were taken of the interface between the oxidised and reference surfaces (fig. 1) and of the oxide film remote from the interface (fig. 2). Considerable detail is visible, and in particular it can be seen that the oxide film is ridged and that occasionally the oxide breaks away from the metal substrate at the places indicated by arrows in figs. 1 and 2. This behaviour is of obvious importance in electronic component manufacture and it would therefore be of interest to examine the conditions for good and bad adhesion of the oxide to the substrate.

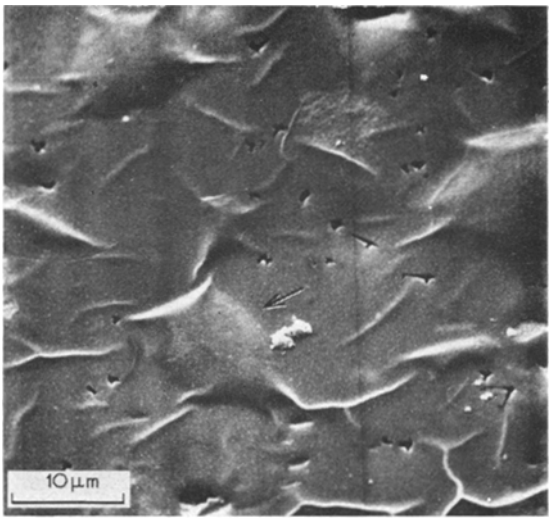


*Figure 2* Oxide film in a region remote from the interface.

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