decreased, or vice versa, these changes do not necessarily occur at the same rate for all faces. The relative rates of incorporation at the different faces would then change as the solution composition changed.

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Development of mechanical strength in hot-pressed silicon nitride

Alpha-silicon nitride, when hot-pressed with magnesia as an aid to densification, shows anomalous strength development behaviour in that its room temperature modulus of rupture (M O R) continues to increase with hot-pressing time after the completion of densification [1]. This increase is known to be linear with time up to a maximum of approximately 800 MNm^{-2}, after which continued hot-pressing leads to a reduction in strength.

Several explanations for the strength increase have been put forward, including the removal of large microstructural features during prolonged hot-pressing [1] or the removal of traces of closed porosity by a mechanism involving α- to β-silicon nitride phase transformation [2]. Material prepared from a starting powder containing a high proportion of α-silicon nitride has been shown [3] to have twice the strength and a fracture energy four times as great as material hot-pressed from powder with a high β-content. The greater fracture energy of the hot-pressed α-silicon nitride has been attributed to the formation, during hot-pressing, of lath or fibre-like grains thus increasing the frictional interaction between grains during crack propagation. It is believed [4–6] that the high-temperature strength of hot-pressed α-Si_3N_4 may also be enhanced by an increased grain pull-out contribution of fibre-like grains to the crack propagation stress.

The purpose of the present work is to investigate further, the post-densification development of strength of hot-pressed α-silicon nitride containing magnesia. Accordingly, the room temperature M O R has been measured on a number of samples of α-silicon nitride hot-pressed to theoretical density and then subjected to continued hot-pressing or to subsequent heat treatment without applied pressure.

Discs, 25 mm in diameter, were hot-pressed, as described elsewhere [7], from high purity silicon nitride* containing 94% of the α-phase. Each disc was diamond machined into six bars of dimensions 2 mm × 2 mm × 22 mm. The longest faces of the bars were ground by hand with 1200 mesh silicon carbide powder on a flat glass plate to impart an even surface finish. The room temperature M O R was determined in three-point bending using fixed steel knife-edges of 19 mm span in an Instron model 1026 testing machine operating at a cross-head speed of 0.5 mm min^{-1}. α- and β-silicon nitride contents were measured by X-ray diffractometry [8]. Thin foil specimens and fracture surfaces were examined respectively by high voltage transmission electron microscopy† and scanning

[*] Plessey Co. Ltd., Allen Clark Research Centre, Caswell, Towcester.
[†] AEI EM7 microscope at British Steel Corporation Swinden Laboratories, Rotherham.

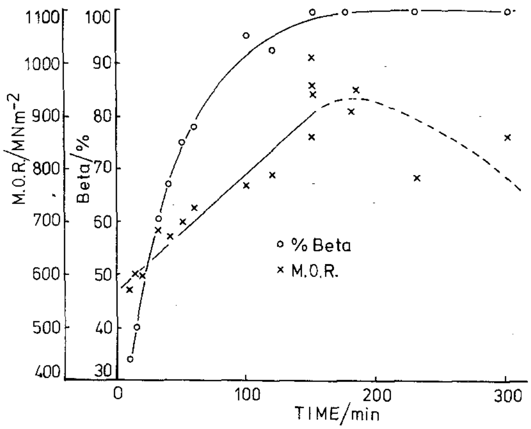

Figure 1 Room temperature modulus of rupture and degree of conversion as a function of hot-pressing time at 1650° C under 20 MNm^{-2} for high α-silicon nitride + 5 wt % MgO.

electron microsopy.

Fig. 1 shows the variation in room temperature strength with hot-pressing time of silicon nitride hot-pressed with 5% MgO at 1650° C at a pressure of 20 MNm^{-2}. Under these conditions observable densification ceased within 3 min at a density of 3180 ± 20 kg m^{-3}. The strength is seen to increase approximately linearly with time from 600 to 900 MNm^{-2} over a hot-pressing period of 3 h after which continued hot-pressing results in a slight decrease in strength. Each point on the graph is the mean of six strength measurements for which the coefficient of variation was 5 to 15% of the mean, as is usually found for brittle fracture [9]. The spread of the means at 150 min hot-pressing time (Fig. 1) is a consequence of the magnitude of this variation.

Superimposed on the strength/time plot is a curve showing the increase in β-silicon nitride content with hot-pressing time for the same samples. The absence of further increase in strength once the α to β conversion is complete suggests that the two phenomena are related. Since it has been shown [8, 9] that the α–β conversion is unaffected by hot-pressing pressure, it follows that the increase in strength with time should also be pressure-independent. To test this hypothesis, samples were hot-pressed at 1650° C to attain full density, and then further heated at this temperature without pressure in order to complete the conversion. These strengths were found to be similar to those of specimens maintained under pressure for the same period. Furthermore, specimens hot-pressed to maximum density at different temperatures had similar strengths, within experimental error, provided their α:β ratios were the same. Microstructural examination of fully converted specimens showed them to have a highly acicular grain morphology (see Fig. 2) similar to that reported by other workers [3, 5] for high strength hot-pressed silicon nitride.

Whereas at high temperatures the presence of elongated grains in hot-pressed silicon nitride may result in an enhanced grain pull-out contribution to the crack propagation stress, due to softening of a glassy intergranular bonding phase, this is unlikely to occur during fracture at room temperature when the grain boundary phase cannot readily

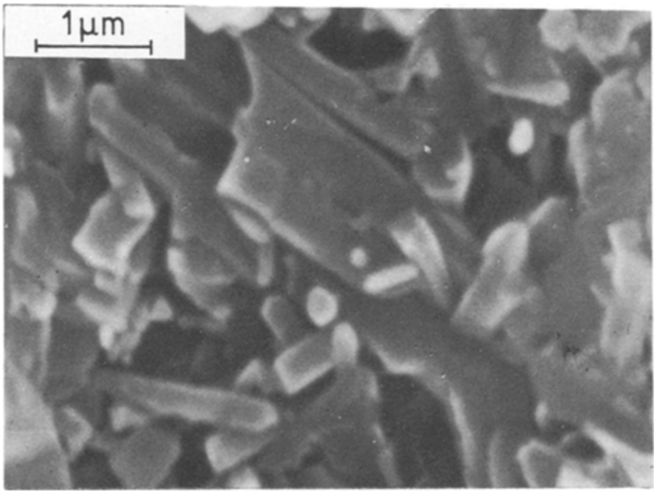

Figure 2 Scanning electron micrograph of fully converted silicon nitride showing acicular grain morphology.

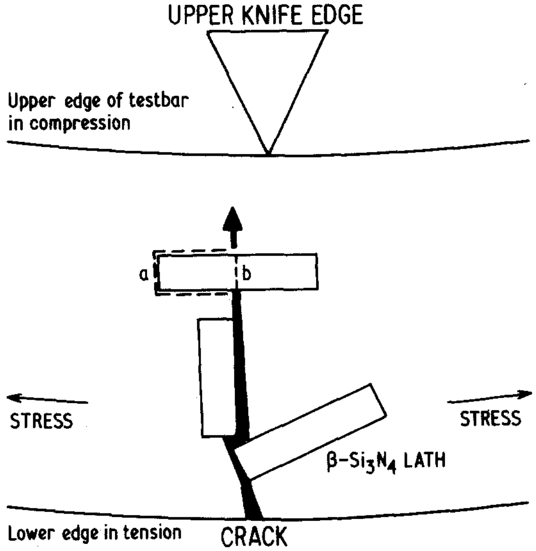

Figure 3 Schematic diagram of possible strengthening mechanism. When the crack reaches a suitably-oriented, elongated grain, two paths for further propagation are possible: either (a) via a long, low-energy grain boundary route involving crack propagation in the direction of the applied stress (a difficult process); or (b) across the grain. Both processes will increase the fracture stress.

flow, and an alternative strengthening mechanism is required. One possible mechanism is illustrated schematically in Fig. 3. Although some preferred orientation exists within the hot-pressed compacts [3, 10], most of the elongated β-phase grains will be oriented at random with respect to the hot-pressing direction and to the axis of the M O R test piece. Some of the grains will be aligned by chance with their long directions perpendicular, or almost perpendicular, to the direction of crack propagation during fracture. Thus entirely intergranular fracture via a comparatively weak grain boundary phase would involve some crack propagation parallel to the direction of the applied stress, that is, in the direction where the stress available for crack propagation is least. In this case transgranular fracture may occur before the resolved stress becomes great enough for continued intergranular crack propagation, resulting in a higher proportion of transgranular fracture and an increase in strength.

Microstructural evidence for this strengthening mechanism is provided (Figs. 4 and 5) by transmission electron micrographs of cracks introduced, after thinning, into thin foils of fully transformed hot-pressed silicon nitride. Fig. 4 shows the extended grain boundary crack path around elongated grains, postulated for intergranular fracture, whilst Fig. 5 shows an extremely long lath which has fractured across its width in order to permit further crack propagation. Secondary crack formation can be seen at one end of this elongated grain.

In summary, the maximum attainable strength of α-silicon nitride hot-pressed with a magnesia additive is determined by the formation, during transformation to the β-phase, of lath-like grains which inhibit intergranular crack propagation during fracture.

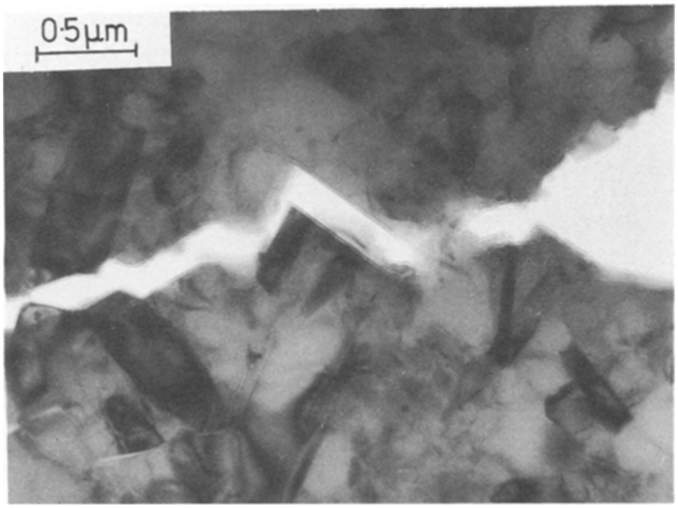

Figure 4 Transmission electron micrograph showing intergranular fracture.

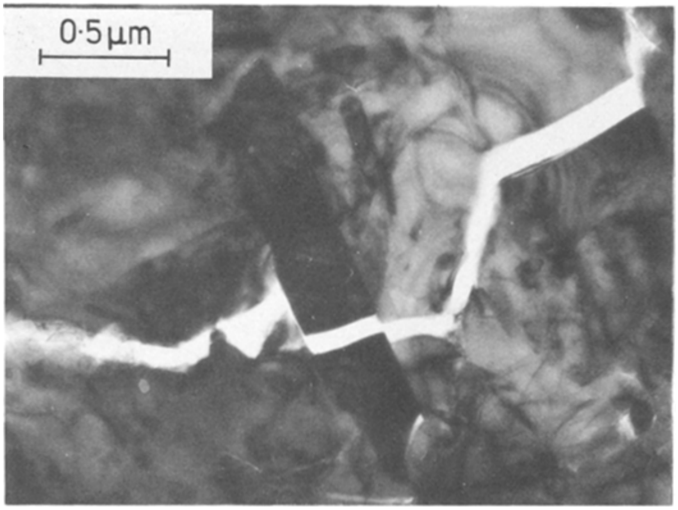

Figure 5 Transmission electron micrograph showing transgranular fracture through long lath-like grain.

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