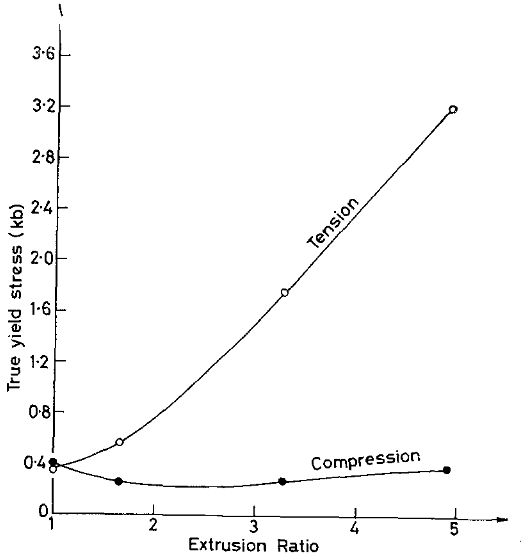

Figure 3 Variation of tensile and compression yield stresses with extrusion ratio $T = 22°$C $\epsilon = 1.7 \times 10^{-3}$/sec.

point on the stress-strain curve which marks the onset of irrecoverable deformation depends in a complicated manner on many variables, and so here we take the first maximum as a measure of the yield stress.

Fig. 3 is a plot of the yield stresses in tension and compression as extrusion ratio. The curves show two distinct regimes.

1. At very low extrusion ratios the compressive strength is greater than the tensile strength. This result is consistent with the reported effect of the hydrostatic component of stress on the yield behaviour of polymers [7] and can be simply interpreted as due to the change in the sign of the hydrostatic component between the tensile and compression tests.
2. At higher extrusion ratios the influence of hydrostatic pressure is overwhelmed by the effects of orientation. The results can be understood in terms of the relative ease of compressing an oriented structure of extended chains compared with extending it further, as we have discussed elsewhere [1].

Further measurements are now being made over a wide range of temperatures and strain-rates to provide data for a more comprehensive understanding of these effects.

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R. A. DUCKETT
I. M. WARD
A. M. ZIHLIF
Department of Physics
University of Leeds
Leeds 2

The nitriding of silicon powder compacts

A versatile route for the production of silicon nitride ceramic is reaction-sintering. Silicon powder (particle size usually < 75 μm) is first formed into a compact by any one of a number of techniques, but frequently by isostatic pressing in the pressure range 50 to 200 MNm^{-2}. The shaped compact is then heated in the temperature range 1250 to 1450°C in a nitrogenous atmosphere when the silicon nitride ceramic is formed. Depending upon the size of the compact being nitrided, sintering times above 120 h can be encountered [1].

It is our object to understand the nitriding mechanism and in particular to identify the reaction rate-controlling process and our starting point is the recognition that the overall nitriding of a compact occurs by the following two steps: (i) the diffusion of the nitrogen-bearing gas into the compact, (ii) the reaction of the nitrogen with individual silicon particles.

Each one of these steps is complex in itself and the second is the subject of another note to be published in this Journal; it is with the gaseous diffusion that we are concerned here.

That gaseous diffusion could be the rate-determining step for compacts above a certain size is self evident and this is intuitively allowed for by the manufacturer. However, a quantitative understanding of this aspect is difficult to achieve because the microstructure of the nitrid-

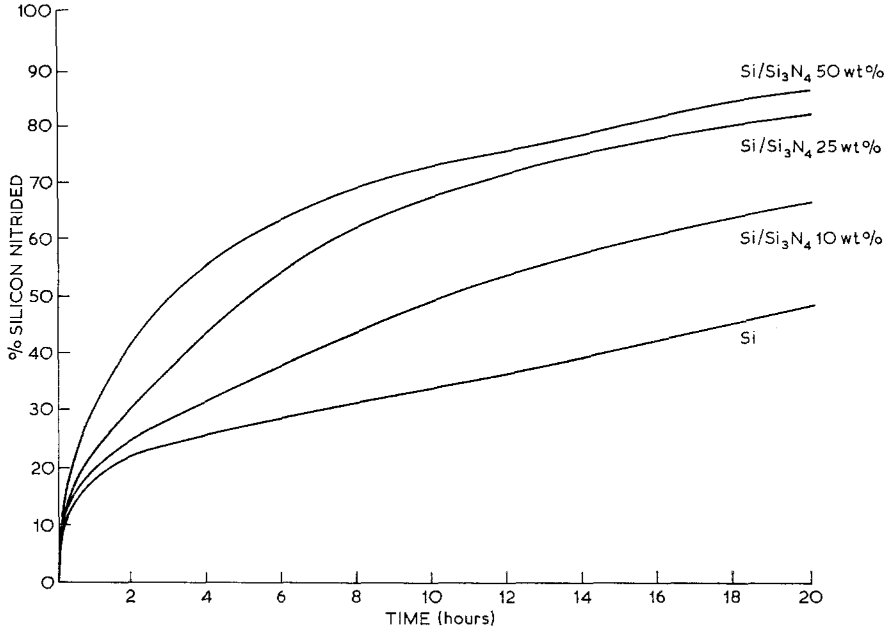

Figure 1 Nitridation curves for Si/Si_3N_4 compacts.

ing compact, and hence its permeability, is continuously changing since:

(i) a volume increase of approximately 22% accompanies the conversion of silicon to silicon nitride and, since there is practically no change in the overall dimensions of the compact, new material formed must be accommodated in the pore system, and

(ii) depending upon the precise nitriding conditions within the compact (i.e. temperature and atmosphere) the crystal morphology of the nitride formed might be very different.

Pore sizes in typical compacts change by between two and three orders of magnitude during the nitriding process. Evans and Davidge [2] found pore sizes in the range 10^{-2} to 10^{-1} μm for the ceramic, starting from compacts of particles of mean size 10 μm. These data are essentially in agreement with determinations by mercury porosimetry made by us. It is interesting to note that the mean free path of nitrogen at 1400°C and 760 torr is 0.6 μm and that therefore the mechanism of gas flow into the compacts may well change as the reaction proceeds.

As part of our programme we have determined on a continuously recording thermobalance, the rates of nitriding (at 1375°C in flowing 99.9% N_2) of cylindrical compacts (30 mm length by 15 mm diameter) of a commercial powder of mean particle size approximately 15 μm, isostatically pressed at 50 MNm^{-2}. A series of compacts was made incorporating a progressively greater percentage (0, 10, 25 and 50 wt%) of silicon nitride (approximately 95% α−) powder. The silicon nitride powder was intended to serve as an inert filler in so far as it would undergo no change in volume as the reaction proceeded. The curves (Fig. 1) show clearly that even with the small compacts used here, gaseous diffusion is the rate-determining step. This type of study is now being pursued further using silicon and inert filler having particle sizes confined to a narrow range.

A parallel investigation aimed at effecting control over the α-Si_3N_4; β-Si_3N_4 ratio in the reacted compact is being made; this stems from our belief that the ratio will be one of the factors determining permeability of the product. In initial experiments (100%) silicon compacts, similar to those referred to above, were nitrided at 1350°C in flowing nitrogen which had been passed through a liquid nitrogen trap to remove water. Also, by passing the nitrogen through a temperature-controlled bed of zirconium turnings its oxygen potential was varied, and measured with a zirconia oxygen-meter in series with the getter. Although the partial pressure of oxygen in the nitrogen could be varied over the range 10^{-4} to 10^{-26} atm, X-ray analysis of the product showed no significant variation in $\alpha : \beta$ ratio from a value approximately 85 : 15. The conclusion drawn from these experiments, in the light of the knowledge that the α-nitride is an oxynitride [3], was that the source of oxygen was most probably a silica layer on the silicon particles themselves. In a subsequent experiment 5 wt % aluminium powder was added to the silicon powder with the object of chemically reducing this silica layer. This brought about a change in the $\alpha:\beta$ ratio in the product to the value 20:80. In the case of the undoped sample ($\alpha:\beta$ ratio 85-15) the overall weight gain in 25 h at 1350°C was 43 %, whereas for the aluminium-doped sample the corresponding gain was 60 %. This would seem to support the view that the change in $\alpha:\beta$ ratio was accompanied by a change in microstructure with an attendant change in permeability.

The initial observations reported here clearly demonstrate the need for detailed studies of these types if the reaction-sintering process is to be fully understood and optimized.

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A. ATKINSON
P. J. LEATT
A. J. MOULSON
Department of Ceramics
University of Leeds
Leeds, UK