Acknowledgements

We are grateful to Dr S. M. Allen for helpful suggestions, critical reviews, and for providing us with Fig. 3.

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Received 22 April
and accepted 18 May 1976

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The influence of hydrogen in the nitriding gas on the strength of reaction sintered silicon nitride

Reaction sintered silicon nitride is usually prepared by heating silicon compacts in an atmosphere of nitrogen which is maintained at a pressure slightly above atmospheric pressure in order to minimize the possibility of air leaking into the furnace. In order to conserve nitrogen, "static" gas systems are used [1, 2] and nitrogen is supplied to the furnace at a rate determined by the rate of consumption of the gas by the reacting silicon compacts. Recent evidence has indicated that whilst contamination of the nitriding atmosphere with oxygen and water vapour has little influence on strength [3], gas flow during nitriding has a significant effect [2]. When nitrogen is allowed to flow through the furnace even at very slow rates the structure of the product is modified, much larger critical defects are formed and small but significant changes in elastic moduli and the surface energy for fracture initiation result [4]. It has been suggested [2] that undetected leaks in nominally "static" nitriding systems could produce sufficient gas flow to adversely affect the strength of the product and that this was a reason for occasional weak batches of reaction-sintered silicon nitride. The detection and elimination of small leaks in large furnaces operating at temperatures up to about 1400°C is a difficult practical problem.

We are studying the influence of hydrogen in the nitriding gas on the strength of reaction sintered silicon nitride and some important preliminary results are reported here. A batch of silicon powder (Table I) was isostatically pressed at 185 $\mathrm{MN\,m^{-2}}$ and the compact heated for 4 h at 1175°C in argon. Test bars 4.57 mm x 4.57 mm x 30.0 mm were machined from the compact and nitrided to various degrees of conversion at temperatures from 1200 to 1350°C under "static" conditions or in a gas flow of 100 $\mathrm{ml\,min^{-1}}$ using either high purity nitrogen or gas mixtures by volume of $99\,N_2/1\,H_2$, $98\,N_2/2\,H_2$, $95\,N_2/5\,H_2$ and $90\,N_2/10\,H_2$. Nitriding conditions were

TABLE I Characteristics of starting silicon powder

Median particle size* (μm)	13
Maximum particle size* (μm)	60
Specific surface area† ($m^2\,g^{-1}$)	1.5
Impurity content (wt %)	
Iron	0.87
Aluminium	0.20
Calcium	0.27
Titanium	0.08
Other cations	0.05
Oxygen‡	1.0

*Measured by Coulter Counter.
†Measured by BET.
‡Measured by neutron activation analysis.

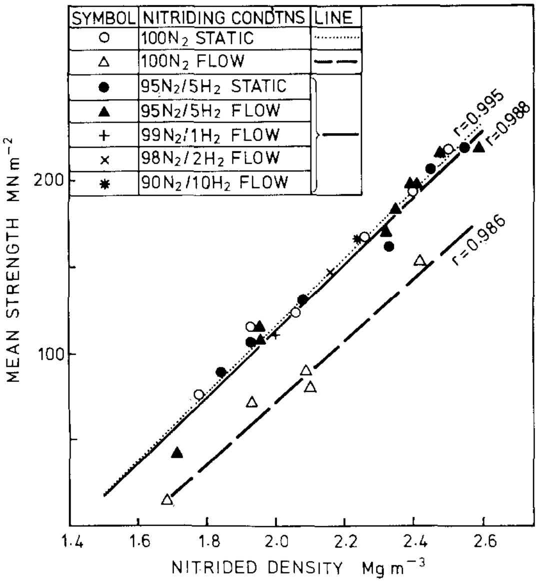

Figure 1 Mean strength as a function of nitrided density for silicon compacts nitrided under various conditions.

in all other respects identical and have been fully detailed elsewhere [2]. Densities were determined from the weights and dimensions of the test bars and their strengths determined in three point bend using a span of 19.05 mm. The results were analysed in terms of the relationship between strength and nitrided density [1] and are summarized in Fig. 1. The dotted line of Fig. 1 is a least squares fit for material nitrided under "static" conditions in a nitrogen atmosphere whilst the broken line represents material nitrided in flowing nitrogen. As previously reported [2–5] much lower strengths result from the "flow" system. The solid line of Fig. 1 is a least squares fit for materials nitrided in gas mixtures of nitrogen and hydrogen under "static" or "flow" conditions. It is clear that the use of nitrogen/hydrogen gas mixtures eliminates the adverse effect of gas flow which results when nitrogen alone is used. This effect appears to be insensitive to the gas composition over the range from 1 to 10% hydrogen, although it is noted that reaction rates are influenced by the gas composition.

In terms of the recently proposed models [3–5] concerning the development of the structure of reaction sintered silicon nitride we suspect that hydrogen influences the proportion of silicon nitride which forms as a continuous network by assisting the vapour-phase transport of the reacting species. The purpose of this communication is, however, to point out that the use of nitrogen/hydrogen gas mixtures may provide a practical means of obviating the adverse effect of gas flow (e.g. small, undetectable leaks) in "static" nitriding systems.

The use of nitrogen/hydrogen gas mixtures has been discussed in a different context by Mangels [6] who reports their beneficial effect in improving both the strength and creep properties of reaction sintered silicon nitride produced under "static" conditions. We have not confirmed that any strength improvement is to be gained by using nitrogen/hydrogen gas mixtures under "static" conditions (Fig. 1) in our particular experimental system, but it may be of significance that Mangels employed a reaction stage above the melting point of silicon (~ 1420° C), in his nitriding schedule. It is well known that lower strengths result when significant nitriding occurs above the melting point of silicon [7, 8] and this may account for the relatively low strength reported by Mangels for material nitrided in "static" nitrogen. We have noted that the use of nitrogen/hydrogen gas mixtures can greatly enhance the rate of nitridation, so the improvement in strength obtained by Mangels with the nitrogen/hydrogen gas mixture might be a consequence of an increase in the degree of conversion which occurs below the melting point of silicon.

The results of a detailed investigation of the influence of nitrogen/hydrogen gas mixtures on the structure and mechanical properties of reaction sintered silicon nitride will be published in due course.

Acknowledgments

Thanks are due to B. Luxton, W. May and J. Studley for experimental assistance. This note is published by permission of the Controller, HMSO, holder of Crown Copyright.

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Received 26 April
and accepted 28 May 1976

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Small-angle X-ray scattering of polyethylenesulphide fibres

In a recent paper, Hendra and Majid [1] have used the Raman method to show that polyethylene sulphide, being a highly crystalline material, forms lamellar crystallites and that these lamellae thicken on annealing as function of temperature. Apparently attempts to prove the lamellar structure by small-angle X-ray diffraction observations so far have been unsuccessful [1].

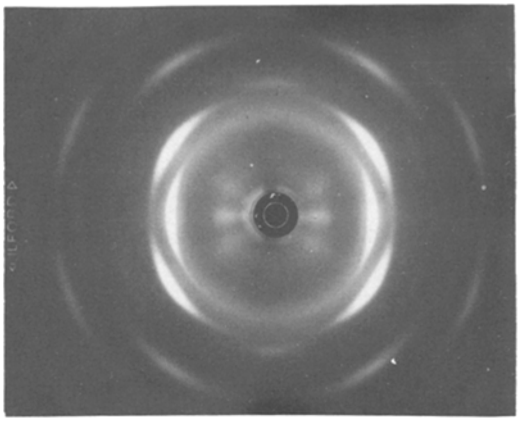

Figure 1 Wide-angle diffraction pattern of spin-oriented polyethylenesulphide fibre. Ni-filtered Cu$K\alpha$ radiation. Sample to film spacing, 5 cm.

In the course of melt spinning studies leading to oriented crystalline fibres (spin-orientation) we have produced a polyethylene sulphide morphology completely analogous to that of a spin-oriented polypropylene [2], i.e. we observe a fan-like meridional SAXR diffraction pattern in the range from 60 to 140 Å, the centre being at about 75 Å (Fig. 2a). The orientation of the crystallites is quite good, as shown in the wide-angle X-ray pattern of Fig. 1. (Similar to the sample prepared by Y. Takahashi *et al.* [3].)

On annealing these samples between 140 and 180° C for 1 h, the small-angle pattern changed considerably, the long fan-like spacing breaking into two meridional spots, the outer one increasing from 82 (140° C) to about 100 Å (180° C), the inner one being much sharper and having small lateral dimensions (Fig. 2b and c, 160, 180° C).

From comparison with polypropylene [2], there is no doubt that the meridional scattering is based on a lamellar structure, the lamellae showing a range of thicknesses and being arranged normal to the extrusion direction. However, in polypropylene, the lamellar fan gradually sharpens on annealing as the lamellae become more uniform; at 135° C and higher a weak overtone becomes visible.

On annealing polyethylenesulphide, the second

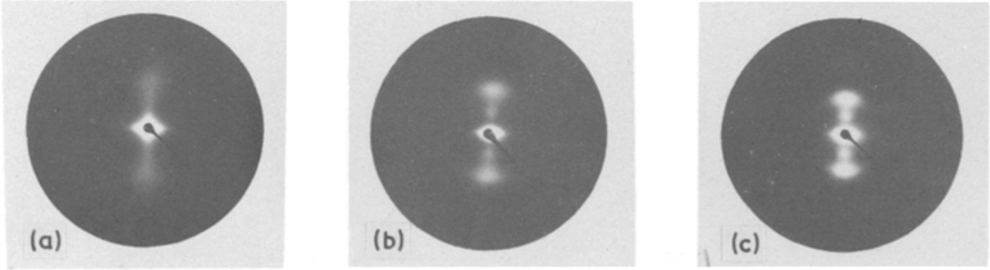

Figure 2 SAXR diffraction pattern of polyethylenesulphide fibres: (a) as-spun, (b) annealed 160° C for 60 min (c) annealed 180° C for 60 min. Ni filtered Cu$K\alpha$ radiation, Rigaku Denki Rotating Anode Generator 100 mA, 50 kV, sample to film 300 mm, exposure 18 to 20 h.