Letters

The α/β-Si_3N_4 question

Several intriguing points are raised in the recent communication by Morgan [1] concerning the α/β-Si_3N_4 question; in particular, it is suggested that the balance of the phase yields is governed predominantly by seeding. Data which may be used in support of the suggestion that the seeding of silicon powder with α- or β-silicon nitride powders should predispose the system to nitride to α- or β-silicon nitride, in fact already exist [2].

Some time ago, in the course of a study of the kinetic factors influencing formation of the α- and β-phases of silicon nitride from a range of silicon powders, we carried out a small number of experiments involving the addition of small proportions of pre-formed α- or β-silicon nitride powders to samples prior to nitridation for 6 h at 1365° C under zirconium gettered nitrogen at 1 atm. pressure. Fig. 1a shows data for one of these powders, powder D [3]. The changes in phase yield after this time suggest that the incorporation of small amounts of α-silicon nitride seed material does indeed switch the balance of product from the β-phase to the α-phase. While the increase in the amount of α-phase formed is consistent with the provision of a higher concentration of α-phase growth nuclei (the importance for the nitridation of appropriate nitride nuclei is established) [4], the simultaneous fall in β-phase yield suggests that the overall growth rate is determined to a certain extent by the rate of supply of silicon vapour. However, the total amount of product-phase increases slightly with increasing α-silicon nitride additions. This is in keeping with previous observations [5, 6], and suggests that the action of silicon nitride additions is rather more complex than simply the provision of growth centres. It would seem that effects in addition to that of seeding need to be explored. The possibility that the addition of silicon nitride powder is in effect the addition of (surface) silica may be discounted; the consequences of the deliberate additions of silica to a silicon powder have been examined and have been shown to lead to distinct falls in product yield [3] over this time scale.

β-silicon nitride seeding shows a less marked effect in the case of powder D. In the absence of additions this powder tended to give a predominance of the β-phase, assumed to be a consequence of iron contamination and therefore the fact that β-silicon nitride seeding does not show a large increase in β-silicon nitride product is perhaps not surprising. Fig. 1b on the other hand shows that a lower specific surface, high purity powder, powder C [6], which normally produced a high α-phase product, did appear to respond to β-silicon nitride seeding. The higher temperature was used to improve product yields with this lower reactivity powder. Table I provides a summary of the characteristics of these powders.

All these data may therefore tentatively be taken as supporting the view that the phase nature of the initial silicon nitride nuclei is one of the factors determining the final phase yield.

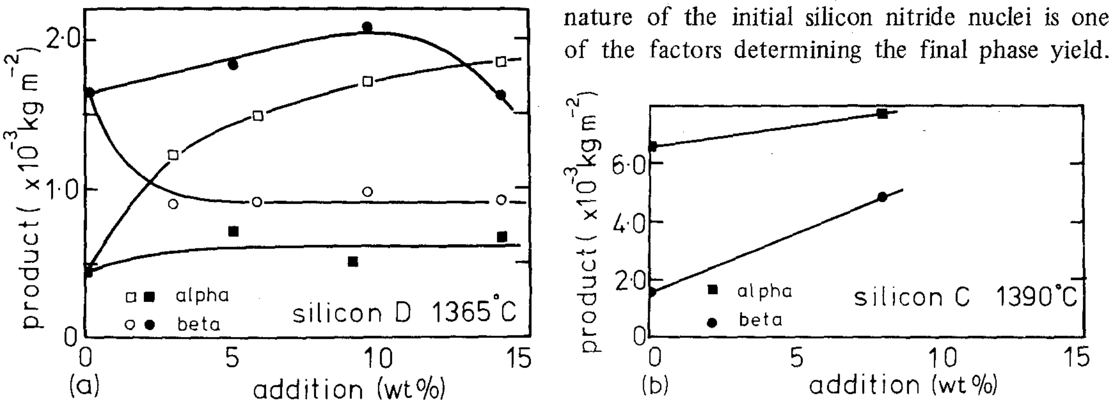

Figure 1 (a) α- and β-silicon nitride yields with additions of α-silicon nitride powder (hollow symbols) or β-silicon nitride powder (filled symbols) to silicon powder D before nitriding at 1365° C. (b) α- and β-silicon nitride yields with additions of β-silicon nitride powder to silicon powder C before nitriding at 1390° C.

0022-2461/80/092385-02$02.20/0

TABLE I

Powder	Specific surface area ($m^2 kg^{-1}$)	Metallic contamination (at%)	Oxygen content (at%)
C	0.06	0.02	0.33
D	0.21	0.66	0.52

However, because of the existence of secondary effects with the use of silicon nitride powder additions (themselves meriting further study), the *in situ* generation of seeds by suitable preliminary short-term treatment is probably to be preferred as an experimental technique. Contamination of silicon nitride powders by metals or oxygen during milling, for example, is one possible source of uncertainty which this method avoids.

We would not hold, however, that the crystallographic form of the nitride nuclei is the only factor determining the phase of the silicon nitride grown. As indicated by Morgan, liquid phases, such as liquid silicon or metal silicon alloys, play a part in the formation of β-silicon nitride, and correlations exist between the extent of β-phase formation and the iron contamination level of a silicon powder [7] through nitridation under nitrogen (though not nitrogen–hydrogen mixtures) [8]. To what extent this is the result of a solution-reprecipitation process, or as a result of the provision of a suitable medium for the direct growth of the β-phase from dissolved nitrogen needs to be established by precise kinetic measurements of the α- to β-phase conversion rates in the presence of appropriate liquids. Data for the conversion rates at a much higher temperature (1600° C), under a nitrogen pressure of 1 atm. and with relatively large volumes of a magnesium silicate liquid, have been published [9], but it is difficult to make extrapolations of reaction rates from this set of conditions to those normal for the nitridation process.

Acknowledgements

This study was supported by grants from the Spanish Association of Mining Engineers and from UNESCO.

References

1. P. E. D. MORGAN, *J. Mater. Sci.* 15 (1980) 791.
2. D. CAMPOS-LORIZ, Ph.D. Thesis, Department of Ceramics, University of Leeds, 1976.
3. D. CAMPOS-LORIZ and F. L. RILEY, *J. Mater. Sci.* 11 (1976) 195.
4. A. ATKINSON, A. J. MOULSON and E. W. ROBERTS, *J. Amer. Ceram. Soc.* 59 (1976) 285.
5. A. ATKINSON, P. J. LEATT and A. J. MOULSON, *J. Mater. Sci.* 7 (1972) 482.
6. R. J. LUMBY, U.S. Patent Number 3591337, 10 April 1967.
7. D. CAMPOS-LORIZ and F. L. RILEY, Proceedings of the Conference on Science of Ceramics, No. 9, (Nederlandse Keramische Vereniging, Stock-on-Trent, 1977), p. 38.
8. H. DERVISBEGOVIC and F. L. RILEY, *J. Mater. Sci.* 14 (1979) 1265.
9. D. R. MESSIER, F. L. RILEY and R. J. BROOK, *J. Mater. Sci.* 13 (1978) 1199.

Received 14 April
and accepted 12 May 1980.

D. CAMPOS-LORIZ
F. L. RILEY
Department of Ceramics,
University of Leeds,
Leeds LS2 9JT, UK