Letters

Factors affecting the formation of the α- and β-phases of silicon nitride

A study has been carried out into the nitriding behaviour of several grades of commercial silicon powder to try to determine the reasons why different powders yield different proportions of α- and β-silicon nitride when nitrided under identical conditions [1]. In particular, attempts have been made to identify the basis of the effects previously reported [2, 3], whereby metallic impurities in the silicon powder, or in the nitriding atmosphere, appear to favour formation of the β-phase of silicon nitride. It has been noted that under the highest purity conditions α-silicon nitride tends to be formed almost exclusively [4].

We report here results obtained with two silicon powders of similar chemical purity, but of different particle size ranges. The characteristics of the powders are shown in Table I. If the assumptions are made that the silicon has a surface silica film of the order of 3 nm thick, and that the metals are present as oxides with iron in the Fe (III) state, then, within the analytical errors, all the oxygen in powder A can be accounted for, and it appears that powder B contains some 0.9 wt % of additional silica.

Nitridation conditions for the small (approximately 10 mm diameter × 10 mm length) silicon powder compacts were identical with those described previously [3]. Experiments were carried out at temperatures in the range 1305 to 1400° C for a fixed time, normally of 6 h. Data concerning the amounts of the two product phases formed at each temperature are presented in Fig. 1, plotted for convenience in Arrhenius form. The term Pr/100 Si refers to the weight of α- or β-phase formed from 100 units of weight of silicon.

It can be seen that at temperatures below 1350° C both the α-phase and the β-phase forming reactions obey Arrhenius relationships. The fall-off in extent of reaction for powder A at higher temperatures can be attributed to partial melting of the powder caused by the fast exothermic reaction. The nitridation behaviour of powder B at 1365° C has been discussed elsewhere [3] and it is clear that the pattern previously identified is characteristic of its behaviour over a wide range of temperature with the β-phase forming acceleration occurring earlier with increasing temperature. Further evidence is also provided of the important involvement of the alumina reaction tubing (types designated A and B) on the course of the nitridation reaction.

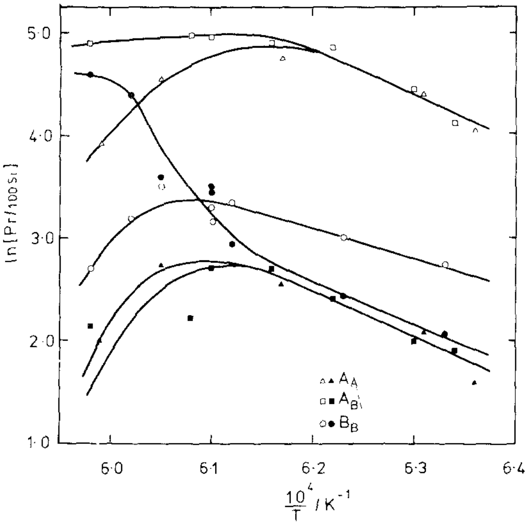

Figure 1 Plots of natural logarithm of product yield from powders A and B at 6 h as a function of reciprocal temperature. Solid symbols indicate β-phase. Subscripts A and B refer to the type of alumina furnace tubing used.

The main points of interest in the present study concern the lower temperature region. Here the initial formation rates of the β-phase are

TABLE I Characteristics of silicon powders A and B.

Powder	B.E.T. surface area ($m^2\ kg^{-1}$)	Median Stoke's diameter (μm)	Impurity element content (at. %)							Estimated surface oxygen (as a 3 nm silica film) (at. %)
			Al	Ca	Fe	Mg	K	Na	O	
A	2150	2.7	0.58	0.04	0.30	0.004	0.003	0.002	2.45	1.32
B	500	23	0.69	0.04	0.38	0.006	0.012	0.005	2.80	0.31

closely similar for both powders. On the other hand, the rate of the α-phase reaction is of the order of 4.5 times faster for powder A, compared with that for powder B. This ratio is very close to that of the specific surface areas of the two powders. These points provide further evidence that the α- and β-phase forming reactions must be regarded as two distinct processes, and need to be studied accordingly.

We have suggested [3] that formation of the α-phase of silicon nitride can be associated with the presence of silicon monoxide in the nitriding compact, and with the use of oxygen as a silicon carrier through the reaction

$$\mathrm{Si(s)} + \tfrac{1}{2}\,\mathrm{O_2(g)} \longrightarrow \mathrm{SiO(g)} \qquad (1)$$

The fact that the rate of the α-phase forming reaction appears to be related to the surface area of the silicon would be consistent with the involvement of Reaction 1 in the rate-controlling process. The rate of supply of silicon vapour by direct evaporation from an exposed silicon surface would also be surface area dependent. However, because of the further reaction

$$\mathrm{Si(g)} + \mathrm{SiO_2(s)} \longrightarrow 2\mathrm{SiO(g)} \qquad (2)$$

silicon vapour would be rapidly converted to silicon monoxide as long as silica was present in the system (the equilibrium partial pressures at 1650 K are 4×10^{-7} atm and 6×10^{-3} atm respectively [5], and can probably be discounted as a nitriding gas phase species at this stage of the reaction.

In the case of the β-phase forming reaction it is necessary to look for points of similarity between the two powders, and the levels of metallic contamination must be regarded as the probable significant feature. Because of the apparent insensitivity of the reaction rate to the total surface area, it must be assumed that β-phase formation takes place predominantly at impurity-rich sites, the concentration of which will be similar for both powders. It would be expected that aluminium-rich inclusions [6] would generate the β′-sialon phase [7]. Because the aluminium is incorporated into the nitride crystal structure, however, this is a process which will diminish in importance with time. Further experiments, involving variations in the quantity of iron present in powder B, suggest that iron may also be an important direct factor assisting the β-phase forming reaction. It would moreover be a continuous factor because, unlike aluminium, iron would not be progressively absorbed by the nitride. Data presented in Fig. 2 show that, while increasing the iron content of powder B has only a slight effect on the β-phase forming reaction, a reduction in the iron content achieved by acid washing has a considerable effect on the β-phase reaction. Alumino-silicate phases, or α-alumina, would not be expected to be appreciably soluble under the wash conditions used (1M HCl at room temperature). The implication is that iron present at the silicon surface, introduced for example during milling, is far more effective in generating the β-phase. Iron added later and separated from the silicon by the silica film is relatively inactive, although it appears to inhibit to a certain extent the α-phase forming reaction. Because silicon will reduce any oxide of iron to the metal, and since the solidus temperature in the Si–$\mathrm{FeSi_2}$ system is 1212° C [8], iron initially present at the silicon surface will form a liquid phase under nitriding conditions. The further implication therefore is that growth of the β-phase at this stage of the reaction occurs predominantly at liquid metal–silicon alloy sites. A similar conclusion, that the β-phase formation is enhanced by the presence of a liquid iron–silicon alloy, has also been reached independently from detailed studies of the nitridation of high purity silicon, doped with iron up to 0.25 at.% [9].

The present study indicates the direct involvement of metallic impurities in the formation of β-silicon nitride during the early stages of nitridation. Earlier work [3] pointed to the possible indirect action of metallic impurities, as an influence on the stability of the native silica

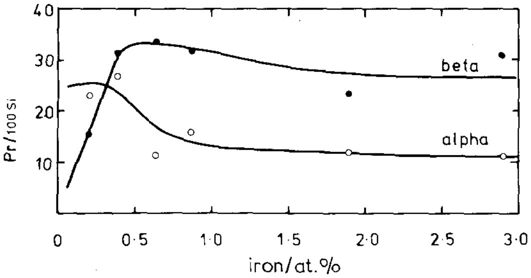

Figure 2 A plot of product yield from powder B after 6.5 h at 1365° C (alumina B), versus iron content.

film, an effect confirmed in the case of iron both for the oxidation of silicon, and in the nitridation of high purity silicon [9, 10]. Further work is now needed to clarify the origins of the later, faster, "β-stage" process responsible for large scale β-silicon nitride formation in powder B [3]. This was assumed earlier to be due to an enhanced release of silicon vapour from a clean silicon surface. The possibility now needs to be examined that this feature is due to a liquid phase reaction consequent upon the rapid, widespread, wetting of silicon surfaces free from silica.

Acknowledgements

The assistance of H. P. Rooksby in the interpretation of X-ray diffraction data is gratefully acknowledged, as are the support grants from UNESCO, and the Spanish Association of Mining Engineers, to D. Campos-Loriz.

References

1. D. CAMPOS-LORIZ, Ph.D. Thesis, Department of Ceramics, University of Leeds (1976).
2. R. B. GUTHRIE and F. L. RILEY, *J. Mater. Sci.* 9 (1974) 1363.
3. D. CAMPOS-LORIZ and F. L. RILEY *ibid* **11** (1976) 195.
4. R. B. GUTHRIE and F. L. RILEY, *Proc. Brit. Ceram. Soc.* **22** (1973) 275.
5. JANAF, Thermochemical Tables, 2nd edition, NBS (1971).
6. D. J. GODFREY, Society of Automotive Engineers Paper No. 740238, New York (1974).
7. K. H. JACK, *J. Mater. Sci.* **11** (1976) 1135.
8. M. HANSON, "The Constitution of Binary Alloys" (McGraw–Hill, 1958).
9. S. M. BOYER and A. J. MOULSON, *J. Mater. Sci.* (to be published).
10. S. M. BOYER, D. SANG and A. J. MOULSON. "Nitrogen Ceramics" edited by F. L. Riley (Noordhoff, 1977) p. 297.

*Received 31 August
and accepted 14 October 1977.*

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A new compound in the Ge–Te system

The Ge–Te phase diagram as described by Klemm and Frischmuth [1] has just one compound, GeTe, which has a range of stoichiometry [2]. Its structure has been described [3–5] using a rhombohedral cell with $a = 5.96$ Å, $\alpha = 88°16'$ and $Z = 4$, derived by small distortions of a basic NaCl fcc structure. Stoemenos *et al.* [6] have shown that further structural distortions exist resulting in a doubled cell edge and giving a rhombohedral cell containing ideally 32 Ge and 32 Te atoms. These authors also suggest that the vacant Ge sites, which are implied by the small Ge deficiency always found for low temperature GeTe, may be accommodated along the antiphase domain boundaries present in thin films of the material. While studying the eutectic between GeTe and Te, a new compound has been found and is described here.

15 g batches, prepared from the pure elements with nominal concentrations 15, 16.5, 17.5, 19, 20, 21.5, 22.5 at.%Ge, were melted in evacuated sealed silica tubes at 950° C in a horizontal rocking furnace. Oxidation and volatilization were assumed to be minimal. After quenching and crushing, the specimens were subdivided into five and remelted under the same conditions to ensure homogeneity. The quenched glassy specimens were heat treated at five temperatures in the range 170 to 400° C for 24 h, again in evacuated sealed silica tubes, and then examined by reflected light microscopy and X-ray powder diffractometry.

For samples of composition 20% Ge–80% Te crystallized at 300° C and higher, the diffractometer traces showed GeTe and Te peaks as expected, but treatment at 180° C gave a completely new powder pattern shown in Table I. The appearance of the sample in reflected light is shown in Fig. 1 and can be easily distinguished from the normal GeTe/Te crystals shown in Fig. 2. A sample heat treated at 240° C showed no X-ray evidence of the new phase but using a reflected light microscope it was discovered in small amounts developing as surface crystallization, a characteristic of the 20% Ge–80% Te composition. The new phase was also found in the specimen 19% Ge–81% Te, often nucleated internally, and was present in quantities below