Figure 3 The formation of Ca_3SiO_5 with the addition of various mineralisers. The XRD line intensity ratio has been used.

TABLE II The time after which the first $M_{23}C_6$ carbides precipitated at grain boundaries were observed

Ageing temperature (° C)	Time (sec)	Ageing temperature (° C)	Time (sec)
500	7800	800	5−10
600	1800	900	2−5
700	30−40	1000	1−5

various mineralisers were introduced in a platinum vessel in a Quench Furnace (Stanton-Redcroft) at the sintering temperature (retention time = 1 h; air-quenched).

The kinetics of formation of C_3S are rapid when Al_2O_3 + MgO are added in addition to CaF_2.

LiF appears to boil off from the batch at higher temperature.

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On a growth mechanism for β phase silicon nitride

Boyer and Moulson have recently published [1] some very interesting results concerning the complicated reaction between silicon and nitrogen.

The further clarification of the influence of many nitriding variables and impurities such as oxygen and iron is indeed welcome. It is also pleasing to see further evidence, along with other recent work [2], supporting the idea that the α- and β-phases do form by reactions which can be both kinetically

and mechanistically separated, an idea first suggested by Jennings and Richman [3].

Boyer and Moulson [1], however, suggest a mechanism for the formation of the β-phase which is different from that suggested in [3], and further say that the latter mechanism is "not viable". They say that the β-phase grows into a liquid, and that the liquid is a necessary part of the formation process. The purpose of this letter is to comment on the supposed necessary role of a liquid and on the viability of the present authors' model.

There is no disagreement on the morphology of the β-phase as it grows into grains of impure silicon, the main contaminant being iron. (Incidentally, as double checked by neutron activation analysis, the dirtiest powder used in experiments reported in [3] contained no more than 1.61% cation impurity, not the 12% suggested in [1].) It appears to be angular "spikes" which grow from the edge of a grain towards the interior. This requires that the reaction forming silicon nitride takes place at the terminus, thereby extending its length. Nitrogen, therefore, must be supplied to this reaction site and it is in this aspect of the reaction mechanism that the two models differ. Jennings and Richman suggest that nitrogen diffuses down the large hexagonal tunnels of the z-direction of the β-phase and Boyer and Moulson suggest that the high solubility and diffusivity of nitrogen in the liquid phase, probably $FeSi_2$, provides the probable path that nitrogen takes to the reaction site. They say that the present authors' model is not viable because (i) it is based in part on an earlier model [4] which has since been shown to be incorrect [5], and (ii) their observation that liquid is always associated with β-phase formation is sufficient to make it a necessary and integral part of the formation process.

Firstly, the present authors interpreted the earlier mechanism [4], which involved void formation by diffusion of silicon, as only associated with the formation of α-phase (though the mechanism was not specifically developed for α-phase formation their product was between 70 and 90% alpha and, therefore, most of the important observations were for α-phase formation) and therefore it has nothing to do with our model for the formation of the β-phase. Secondly, as already stated [3], the idea that melting can encourage the formation of β is in no way inconsistent with our model. It was

stated [3] that "the presence of impurities (particularly iron) in the powder will reduce the melting point of silicon and thereby encourage (because of contraction on melting and ability to flow) the formation of the β modification. This is consistent with the observation, both elsewhere and in this study, that impurities can increase the percentage of β-phase in the product". It was stated several times that the formation of β-phase is favoured above the melting point of silicon.

While the present authors do not wish to suggest that Boyer and Moulson's mechanism can never operate, we would like to examine the relative merits of the two possibilities. A schematic representation of the two models is shown in Fig. 1. At the temperature at which nitridation is carried out, the area surrounding β-phase may well be liquid. The β grain is relatively long and thin with the long direction towards the centre of the grain. It is reasonable, then, to assume that β grows into the unreacted material. Nitrogen must, therefore, be supplied to a reaction site which is furthest away from the nitrogen supply, i.e. the gas environment.

Boyer and Moulson suggest that nitrogen is supplied to the reaction site through the liquid surrounding β, route A in Fig. 1. In order to explain the morpohology it might be considered that nitrogen is dissolved in the liquid and then the reaction starts (this would have to happen after melting and before the reaction started, as nitrogen does not dissolve in solid silicon [6].) The growth habit might be explained because the area near the surface, where the reaction starts, becomes nitrogen-depleted and, therefore, the reaction goes deeper into the liquid in search of nitrogen. It
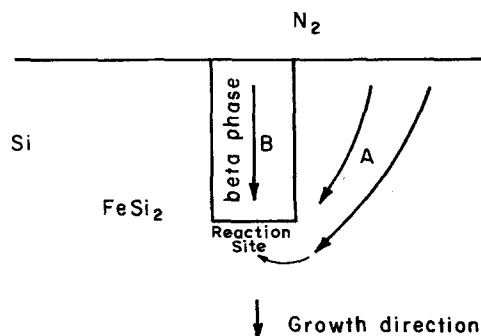

Figure 1 Schematic representation of growth of β-phase Si_3N_4. A and B are possible routes nitrogen can take to reaction site.

seems difficult to imagine that nitrogen, sufficient to form Si_3N_4, could be dissolved in the liquid before the reaction starts. It is interesting to note that the study cited [6] concerning increased solubility states that evidence suggesting that nitrogen dissolves in very pure molten silicon (the only system studied) is the growth of "small amounts" of silicon nitride into the liquid (and always in contact with the nitrogen atmosphere). This observation was only observed when the nitrogen atmosphere was less than 10^{-3} atm. No nitride formed in the liquid at higher pressures.

Alternatively, nitrogen might continue to dissolve in the liquid and diffuse to the reaction site. Here it is difficult to understand why the nitrogen would go the furthest possible distance to reach the tip of the beta grain before reacting. A morphology where a great deal of reaction occurred near the surface would be observed. If long thin spikes were crystallographically preferable they would grow at a shallower angle to the surface. We have never seen this, an observation consistent with the micrograph in [1]. Incidentally, the reference quoted concerning increased diffusivity [7] concerned liquid iron (at 1600° C) with, at most, 10% silicon. Also, 0.02 wt % oxygen or more "markedly lowers the apparent diffusion coefficients" and it was found that diffusivity and solubility are inversely correlated.

One should also consider the problem of the late stages of reaction. As the β grains grow and coalesce, the unreacted inner core becomes smaller, contains less nitrogen, and is more isolated from the nitrogen supply. yet the reaction continues.

The other possibility, which we think is a suggestion which at least warrants further investigation, is that nitrogen diffuses down the β grain itself (path B, Fig. 1). An easy path is provided and it would explain the observed morphology. Here liquid is simply fluid and allows β to grow into it. Liquid can be beneficial as already noted [3].

Finally, it should be noted that recent experiments have shown that reactions strongly favouring the formation of β-phase [8] can occur on semiconductor-grade single-crystal silicon and high-purity nitrogen at 1350° C, well below the melting temperature. Micrographs confirm that melting is unlikely and show large faceted beta grains.

In conclusion, we would like to suggest that although a possible role played by diffusion and dissolution of nitrogen in a liquid could be important under some conditions, it does not rule out other mechanisms. Boyer and Moulson have only shown that increases in iron lead to an increase in β-phase. This does little to elucidate the role that liquid plays in the reaction mechanism. Indeed we would like to say that although liquid is beneficial to the formation of β-phase, it is not necessary.

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