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A mechanism for the nitridation of silicon powder compacts

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A mechanism for the nitridation of silicon powder is proposed, based on an interpretation of the microstructure of partially reacted compacts. It is observed that the reaction does not occur at the solid-state interface between the silicon and the nitride product layer. Both silicon and nitrogen are transported through this layer and the removal of silicon results in the formation of pores in the silicon crystals at the nitride-silicon interface. The nitridation reaction takes place within these pores, which subsequently migrate into the silicon grains, and within the original voidage of the compact.

1. Introduction

Despite extensive study of the reaction between solid silicon and nitrogen the mechanism of the formation of reaction-bonded silicon nitride is still not understood. Thermogravimetric data obtained during the nitridation of single crystals of silicon have not been consistent [1-3] and, indeed, in some cases weight losses have been observed. The kinetics of nitridation of powdered silicon have exhibited variously linear, parabolic and logarithmic reaction rates [4, 5], and the authors have observed kinetics which do not correspond to any of these standard forms [6]. The elucidation of the mechanism from kinetic data alone would, therefore, appear unlikely. Fortunately, the unusual nature of the material provides some incontrovertible facts concerning the reaction, which in themselves impose severe restrictions on the number of mechanisms possible.

Any mechanism proposed must be consistent with the one feature of the reaction which makes the material so attractive commercially – the fact that the dimensions of the compact remain unchanged during nitridation, notwithstanding an increase of approximately 22% in solid volume. It is clear that the extra volume must be accommodated in the original voidage of the silicon compact. On reflection it will be realized that the reaction must, therefore, involve transfer of some silicon into the original voidage *and* movement of nitrogen through the product layer to react with the major portion of the silicon remaining *in situ*. In addition, since the end-product is mechanically-strong, the process must in no way be disruptive.

In the present paper a mechanism is described which complies with these requirements. It is based mainly on observations made on the untypical microstructure of a partially nitrided silicon compact which, fortuitously, disclosed details of the reaction which normally are either not obvious, or are beyond the resolving power of the optical microscope.

2. Experimental

2.1. Nitridation

Cylindrical compacts (15 mm diameter × 30 mm length and density 1480 kg m^{-3}) of 99.99% silicon powder (Koch-Light Laboratories Ltd) were prepared by isostatic pressing at 70 MN m^{-2}. The compacts were first heated in an externally wound, sintered alumina vertical tube furnace in flowing hydrogen at 1350°C for 2 h to remove any oxide from the silicon particle surfaces. The compacts were then reacted in flowing nitrogen at 1350°C. X-ray analysis indicated that more than 90% of the nitride was in the alpha form.

2.2. Specimen preparation

Sections cut from the partially nitrided compacts were mounted in epoxy resin and ground by hand on 600 grade silicon carbide papers with water as lubricant. This gentle preliminary grinding treatment was used to avoid the risk

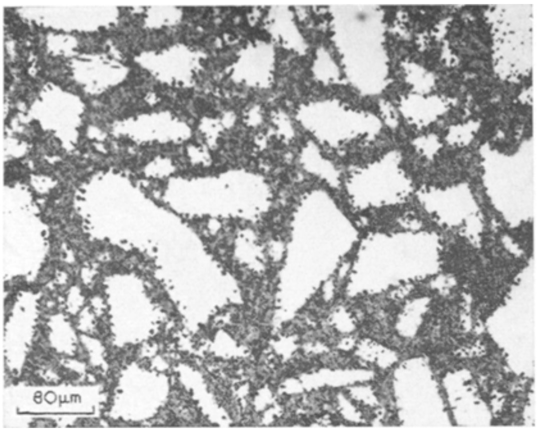

Figure 1 Microstructure in the early stages of reaction (white, silicon; grey, nitride; black, porosity).

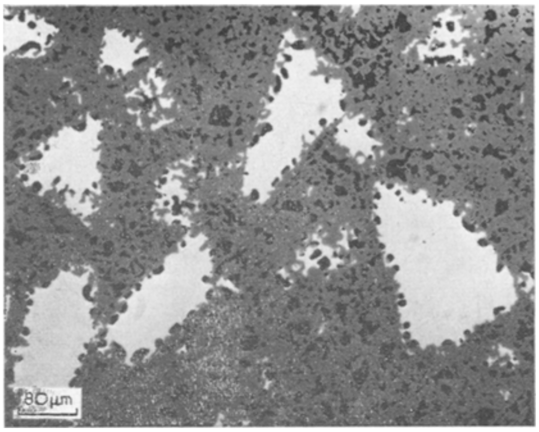

Figure 2 Microstructure when only the large particles are unreacted.

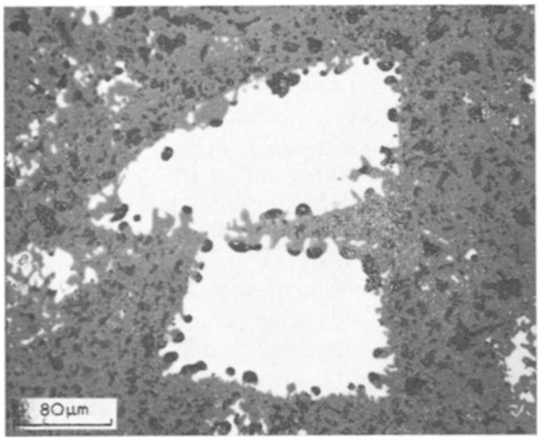

Figure 3 Two particles illustrating that reaction has not taken place at the nitride-silicon interface.

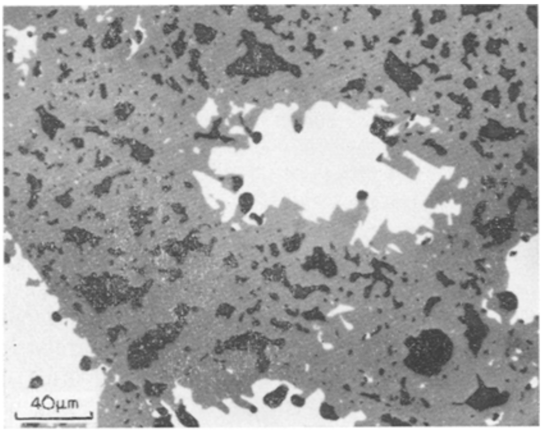

Figure 4 Crystallographic dependence of nitride growth.

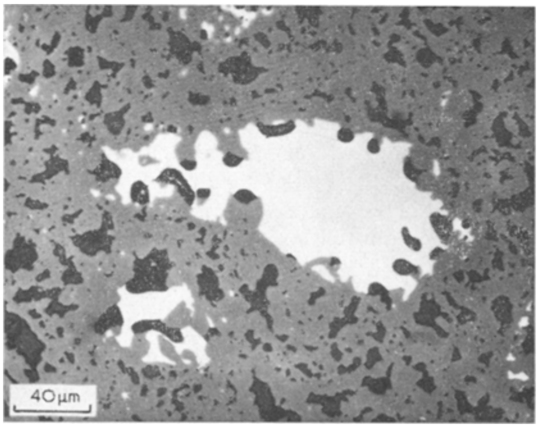

Figure 5 Pores migrating to the centre of a silicon particle.

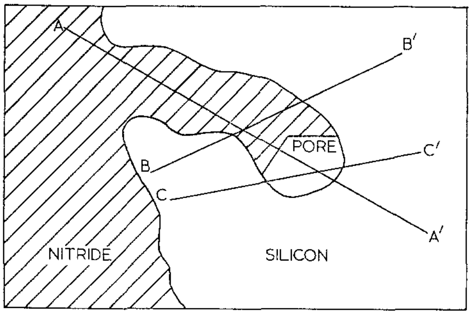

Figure 6 Random sections through the pore-nitride feature which can be seen in Figs. 1 to 5.

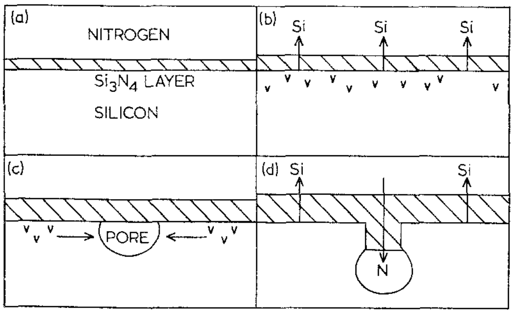

Figure 7 The pore migration mechanism. (a) Silicon is first covered with a layer of nitride. (b) Outward migration of silicon leaves vacancies in the silicon lattice. (c) The vacancies condense to form a pore at the nitride-silicon interface. (d) The nitride grows into the pore and the pore migrates into the silicon particle.

of damaging the porous materials. All the final polishing was performed automatically using 1 μm diamond abrasive on fibre laps.

3. Microstructural observation

Fig. 1 shows the microstructure at an early stage of the reaction and at low magnification. Many small pores (~ 4 μm) can be seen, mainly at the edges of the silicon particles. There is no significance in the fact that some pores appear to be near the centres of silicon particles – it is most likely that the sections are near the upper or lower surfaces of these particles.

Figs. 2 to 5 illustrate a later stage of the reaction when only the larger particles remain unnitrided. From Fig. 3 it can be deduced that:

(a) growth of nitride within the original boundaries of the silicon particles is associated with the migration of pores into the silicon, and

(b) no reaction takes place at the silicon nitride-silicon interface, as evidenced by the original silicon particle boundaries, the position of which can be inferred from the particle contact point.

These observations indicate that the reaction occurs preferentially when one, or both, of the reactants is in the vapour phase.

Fig. 4 shows how migration of the pore, and growth of the nitride, may be influenced by the crystallography of the silicon. It also shows that the silicon was not molten during the reaction. Fig. 5 shows the pore-migration at an advanced stage.

Although the micrographs show both pores and nitride apparently isolated within the silicon, it is believed that these are, in fact, different sections taken through a nitride column coupled to a pore, as illustrated in Fig. 6. This exemplifies the difficulty in relating information obtained from polished sections to the three-dimensional reality.

4. Discussion

4.1. Proposed reaction mechanism

The proposed stages of the reaction are set out schematically in Fig. 7. The initial stage (Fig. 7a) involves the growth of a layer of nitride on the silicon particle. It has been demonstrated that such a layer is formed [7] although the mechanism involved is unknown.

The micrographs clearly indicate that no reaction takes place at the nitride-silicon interface. Therefore, when all the silicon surfaces are covered, the reaction must continue by the outward transport of silicon through the product layer. The nitride forms within the original voidage of the compact thereby maintaining the overall dimensions of the compact. Thus it can be seen that this unique feature of the reaction-bonding process is essentially due to the absence of reaction at the solid-solid interfaces. The outward transport of silicon from the particle results in the formation of vacancies (Fig. 7b) which eventually condense as pores at the nitride-silicon interface (Fig. 7c, cf. Fig. 1).

This cannot be the only mechanism operating, since the original voidage cannot normally accommodate all the nitride so produced. When allowance is made for the 22% volume increase on nitridation, and assuming an initial voidage of 0.4, it follows that the original porosity can accept only approximately 50% of the nitride. Therefore, at least 50% must be formed within the original boundaries of the silicon particles. This necessitates the inward migration of nitrogen through the nitride. From the micrographs it is seen that this reaction takes place at the inner surface of the nitride in the pores which are formed as a result of the outward transport of silicon (Fig. 7c). The nitride grows into the pore by a reaction following the evaporation of silicon (or silicon monoxide) from the surface bounding the pore. Hence the pore migrates into the silicon as shown in Fig. 7d (cf. Fig. 5). Since the nitride occupies a volume greater by 22% than that of the silicon consumed, the pore would eventually close. However, it is possible that it could be maintained by a flux of silicon vacancies from the nitride-silicon interface where the silicon continues to migrate outwards.

4.2. Rate-determining step

The rate-determining step will depend critically on the nature of the nitride layer through which both reactants must pass and, in particular, on the possible existence of microscopic channels in the nitride linking the silicon surface to the nitrogen. If such channels exist the pores would not be formed by vacancy condensation, but by the volatilization of silicon either directly or indirectly as silicon monoxide. The situation is further complicated by the possibility that, after the initial pore formation, the reactions occurring on the inside and the outside of the layer may be independent.

In the authors' opinion it appears to be unlikely that channels could remain open in the presence of silicon-bearing vapour and nitrogen and also unlikely that any such channels could be reopened by a cracking of the nitride (under the influence of stresses incurred during the reaction) bearing in mind that the resulting material is strong. The most likely rate-determining step is, therefore, the solid-state (or grain-boundary) diffusion of both silicon and nitrogen through a "coherent" layer of nitride.

5. Conclusions

The choice of possible mechanisms for reaction-bonding is severely restricted by the well-established fact that no change in overall dimensions occurs during the process even though the volume of solid material increases by 22%. Microstructural examination has revealed that the reason for this effect is that nitridation does not take place at solid-solid interfaces. The reaction involves the counter transport of silicon and nitrogen through the silicon nitride product layer and, within the original boundaries of the silicon particles, the reaction takes place by a pore migration mechanism.

The rate-determining step is not known, but is likely to be solid-state diffusion of the reactants through the product layer.

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References

1. J. W. EVANS and S. K. CHATTERJI, *J. Phys. Chem.* **62** (1958) 1064.
2. M. T. KAMCHATKA and B. F. ORMONT, *Zh. Fiz. Khim.* **45** (1971) 2202.
3. K. J. HÜTTINGER, *High Temp. – High Press.* **2** (1970) 89.
4. D. S. THOMPSON and P. L. PRATT, "Science of Ceramics 3" (Academic Press, London, 1967) p. 33.
5. K. J. HÜTTINGER, *High Temp. – High Press.* **1** (1969) 221.
6. A. ATKINSON, P. J. LEATT and A. J. MOULSON, *Proc. Brit. Ceram. Soc.* **22** (1973) 253.
7. S. N. RUDDLESDEN, "Special Ceramics 1962", edited by P. Popper (Academic Press, London, 1963) p. 341.

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