JOURNAL OF MATERIALS SCIENCE 20 (1985) 3230 - 3238

The influence of iron on the preparation of silicon nitride from silica

S. A. SIDDIQI*, A. HENDRY
Wolfson Research Group for High Strength Materials, Crystallography Laboratory, University of Newcastle upon Tyne, Newcastle upon Tyne, UK

The thermodynamics of carbothermal reduction and nitriding of silica in the temperature range 1200 to 1600° C have been evaluated and may be used to determine the conditions required to form silicon nitride, silicon oxynitride or silicon carbide. The products of reaction are, however, frequently dictated by kinetic rather than thermodynamic considerations and the presence of impurities in the silica and carbon reactants is especially important. α-silicon nitride has been prepared from high purity silica and carbon but under identical conditions of temperature and nitrogen pressure the chemistry of the process changes markedly when a small amount of iron is added to the reactants. Below 1320° C iron has no effect and pure α-silicon nitride is formed but with increasing temperature the proportion of silicon carbide in the product increases. Above 1550° C silicon carbide is the stable solid phase in the Si–C–O–N system at 1 atm pressure. The process chemistry has been investigated by high-temperature reaction studies and X-ray diffraction and reaction mechanisms are proposed on the basis of microstructural observations of reactants and products.

---

1. Introduction

Commmercial production of silicon nitride is by reaction of the elements in a slow, batch process which provides a relatively impure powder unless expensive semi-conductor grade silicon is used. Carbothermal reduction and nitriding of silica is a more rapid process using inexpensive but pure reactants [1] and is now established as one of the most practicable alternatives to the nitriding of silicon as a method of producing high-purity silicon nitride [1–5]. The free energies of formation of α- and β-silicon nitride and silicon oxynitride have been reviewed by Singhal [6], Hendry [7] and Fegley [8] and these data may be combined with tabulated values [9] for other relevant phases to predict the thermodynamic behaviour of the Si–C–O–N system. Calculations of these phase equilibria have been published by Smith and White [10], Rao and Lee [11] and Weiss *et al.* [12] and form the basis of the calculations presented in this paper. The conditions for preparation of silicon nitride from silica by carbothermal reduction and nitriding and the occurrence of other phases in the Si–C–O–N system may therefore be predicted for different conditions of temperature and pressure. The results of Szweda *et al.* [1] show that conversion of silica to α-silicon nitride is complete in 4 h at 1500° C and 10 h at 1400° C and thermodynamic calculations have therefore been carried out at 1 atm total pressure in order to compare theoretical predictions with experimental observations.

Thermodynamic calculation shows, however, only that which is energetically favourable and gives no indication of whether equilibrium will be attained under given conditions or of the relative rates of reaction of the various equilibria

---

**Present address*: Centre for Solid State Physics, Punjab University, New Campus, Lahore-20, Pakistan.

0022–2461/85 $03.00 + .12 © *1985 Chapman and Hall Ltd.*

TABLE I Partial pressures of the principle gaseous compounds in the Si–C–O–N system

Temperature (K)	Partial pressure (atm)			
	p_{N_2}	p_{CO}	p_{SiO}	p_{O_2}
1500	0.34	0.65	0.79×10^{-4}	0.50×10^{-17}
1600	0.59	0.40	0.49×10^{-3}	0.77×10^{-16}
1700	0.79	0.20	0.24×10^{-2}	0.48×10^{-16}
1800	0.88	0.10	0.010	0.24×10^{-16}
1900	0.91	0.050	0.036	0.46×10^{-19}
2000	0.86	0.024	0.110	0.26×10^{-19}

which must be considered. Impurities present in the reactants are also known to play an important role in determining the phases formed and their effects cannot be explained entirely by equilibrium thermodynamics. The present paper shows the calculated equilibrium data and discusses the mechanism of formation of α-silicon nitride by a gas-phase process. The important role of impurities is demonstrated by the effect of small concentrations of iron in the Si–C–O–N system and its relevance to commercial production of silicon nitride is discussed.

2. Equilibrium in the Si–C–O–N system

The equilibrium partial pressure of gaseous phases in the Si–C–O–N system in the temperature range 1500 to 2000 K have been calculated using a method similar to that given by Rao and Lee [11] but which has been modified in two ways. Firstly, the total pressure in the system is fixed at 1 atm to simulate the experimental conditions in a flowing gas and the partial pressures of all gases are then calculated by an iterative method using a set of chemical equilibria sufficient to satisfy the phase rule for the total number of components present. Rao and Lee [11] and Weiss *et al.* [12] give a detailed discussion of this method. Secondly, the present calculation takes account of the formation of α-silicon nitride, β-silicon nitride and silicon oxynitride in calculating the equilibrium partial pressures and uses the thermodynamic data reviewed by Hendry [7] and Fegley [8] rather than the data for "silicon nitride" used by Rao and Lee and Weiss *et al.*

The results of the present calculations differ numerically but not in principle from those of previous authors and are shown in Table I. The partial pressure of carbon monoxide is significant but, with the exception of silicon monoxide (SiO) which will be shown to play an important role, all other partial pressures are negligibly small and are omitted from the table. The value of p_{O_2} is shown in Table I to demonstrate that the calculated value is of the same order of magnitude as that specified for the oxygen-free nitrogen used in the experiments described by Szweda *et al.* [1] and below.

The partial pressures of nitrogen and carbon monoxide presented in Table I have been combined with other relevant thermodynamic data [7–9] to calculate a free energy–temperature diagram as described by Smith and White [10]. The diagram is shown in Fig. 1 where the lines are numbered according to the equilibria which they represent and which are given in Appendix 1 together with the equations used to calculate the values of $RT \log p_{O_2}$. It should be noted that the lines representing the various equilibria are insensitive to changes in the partial pressures of nitrogen and carbon monoxide in the ranges given in Table I. For example in addition to the large uncertainties in the free energy of formation of the nitrides, a change in p_{CO} from 0.2 to 0.8 atm at 1427° C changes the position of line 1 by only 12 kcal, and change in p_{N_2} from 0.8 to

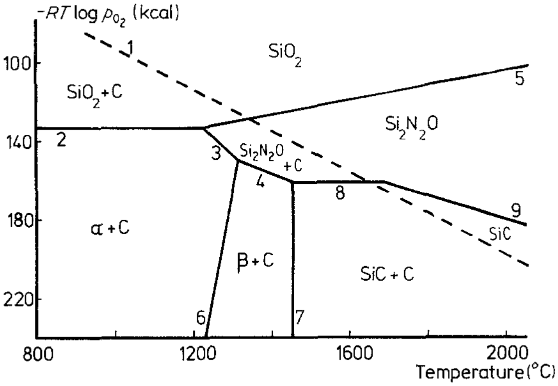

Figure 1 Phase stability in the Si–C–O–N system.

0.2 atm alters the decomposition temperature of β-Si_3N_4 in the presence of carbon from 1460 to 1370° C (line 7). Fig. 1 predicts that at equilibrium the stable phases formed on nitriding $SiO_2:C$ mixtures in the temperature range 1300 to 1500° C will be either β-Si_3N_4 + C or Si_2N_2O + C depending on the oxygen pressure and that at temperatures greater than 1460° C, SiC will form. α-silicon nitride is stable only at lower temperatures. However, the experimental evidence [1–3] shows that when high-purity silica and carbon are reacted in nitrogen the stable phase is α-silicon nitride up to 1500° C above which temperature SiC is formed. In the absence of impurities in the reactants, formations of β and oxynitride is completely suppressed.

These observations appear to be at variance with Fig. 1 but as pointed out by Smith and White [10] diagrams such as this present an incomplete picture of the equilibrium state as no account is taken of gaseous species other than nitrogen, carbon monoxide and oxygen. The partial pressure of silicon monoxide, SiO, is of particular importance and in order to completely represent the equilibrium state the data of Table I for all gas components must be combined with the information on solid phase equilibria in Fig. 1. Such a compilation [10] is extremely complex and is beyond the scope of the present paper but the relevance of SiO to the equilibrium between α- and β-silicon nitride can be demonstrated in a simple manner. The equilibrium between α and β and the major gas species can be represented as

$$2Si_{76}N_{100}O_2 + 2C = 50Si_3N_4 + 2SiO + 2CO \ldots \quad (1)$$

where $Si_{76}N_{100}O_2$ is equivalent to the stoichiometry of α given by Colquhoun *et al.* [13] and accepted by Hendry [7]. Calculation of the equilibrium p_{SiO} for this reaction at the p_{CO} values given in Table I indicates that α should decompose to β above 1300° C. If, however, the p_{SiO} locally within the reacting powder bed is greater than those given in Table I then α remains stable up to the temperature at which SiC becomes stable. It is also well known [1, 2, 4] that reaction of SiO vapour with carbon and nitrogen always produces α and not β. Thus, taking account of the influence of silicon monoxide, the phases observed during nitriding of $SiO_2:C$ mixtures at low p_{O_2} can be explained. If the oxygen potential increases, for example by increasing the $SiO_2:C$ ratio in the reactants below that required to form α, then Si_2N_2O becomes stable. However, it has been shown during the present work that Si_2N_2O will not form unless a liquid phase is present.

The thermodynamic method is therefore not sufficient to predict the phases which occur in the Si–C–O–N system unless all of the reactions involve only solids and gases. There are no liquid phases in this system in the temperature range of interest for production of silicon nitride but small amounts of impurities have a pronounced effect on melting temperatures. Iron is also known to influence both the phases which form and the rates of reaction, and an experimental study was undertaken to investigate this effect as part of a wider study of silicon nitride production from SiO_2 powders.

3. Experimental details

Finely divided fumed silica (Cabosil M5) was mixed with pure carbon black (Cabot Monarch 1300) in a molar ratio of $1SiO_2:4C$ by a sol–gel technique [1, 14]. A colloidal dispersion of solid particles in a liquid is called a sol and under certain conditions it is possible to coagulate a hydrophillic sol to yield a semi-rigid jelly which contains all of the liquid present in the original sol. This product is called a gel. By this technique an extremely intimate mixture of fine particles can be obtained and known concentrations of impurities may be added to the sol before gelation. In the present case iron was added as an aqueous solution of ferric chloride, $FeCl_3$. The $SiO_2:C$ gels were dried in air at 180° C to produce a cake which was easily reduced to fine powder the structure of which has been described by Szweda *et al.* [1]. X-ray photographs show the powder to be amorphous.

The overall reaction for carbothermal reduction and nitriding of silica may be written as

$$3SiO_2 + 6C + 2N_2 = Si_3N_4 + 6CO \ldots \quad (2)$$

The stoichiometric ratio is therefore $1SiO_2:2C$ but a ratio of $1SiO_2:4C$ was chosen to accommodate additional reaction of carbon with combined water in the powder and to ensure that the oxygen potential was maintained at a sufficiently low value.

The experimental technique for nitriding has

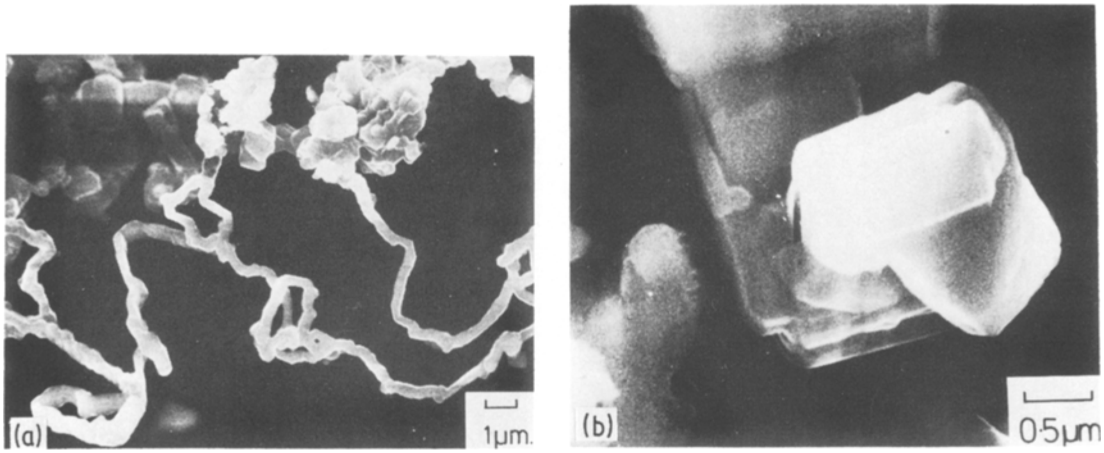

Figure 2 Scanning electron mirographs of crystal shapes of α-silicon nitride in $SiO_2:4C$ pellets nitrided at 1400° C (after Szweda *et al.* [1]).

been described previously [1, 2] and in the present work graphite crucibles were used in all experiments. The products of reaction were characterized by measurement of weight loss during reaction, X-ray diffraction using a Guinier focusing camera with monochromatic Cu*K*α radiation and by scanning and transmission electron microscopy (SEM and TEM). For SEM investigation the powders were supported on graphite substrates and examined in a JEOL JSM-35 microscope. TEM samples were prepared by grinding the reacted power in chloroform placing a single drop of suspension on a holey carbon film and allowing it to dry. Samples were examined on a JEOL 100CX microscope.

4. Results and discussion

When the sample crucible is removed from the furnace after reaction, the exposed inside surface of the graphite crucible and the top surface of the specimen pellet (containing excess carbon) are covered by fine white needles of α-silicon nitride. This product provides clear evidence that the mechanism of formation of α is by a solid–gas mechanism [1] and is therefore in accord with the thermodynamic analysis presented above. The steps proposed for the solid gas reaction are as follows.

(1) SiO is formed by reduction of silica,

$$SiO_{2(s)} + C_{(s)} = SiO_{(g)} + CO_{(g)} \ldots \quad (3)$$

(2) SiO is further reduced by carbon in the presence of nitrogen to produce α

$$76SiO_{(g)} + 74C_{(s)} + 50N_{2(g)} = Si_{76}N_{100}O_{2(s)} + 74CO_{(g)} \ldots \quad (4)$$

Reduction of SiO by carbon to form silicon has a small negative free energy under the conditions given in Table I but simultaneous reaction with nitrogen makes the negative free energy change large and the reaction, therefore, favourable. It has been shown above that α is stable with respect to β under these conditions. SiO may also be reduced to CO

$$76SiO_{(g)} + 74CO_{(g)} + 50N_{2(g)} = Si_{76}N_{100}O_{2(s)} + 74CO_{2(g)} \ldots \quad (5)$$

but the equilibrium p_{CO_2} is very small and this mechanism requires three different gas components to react in an extremely complex stoichiometry which may be discounted on a simple probability basis.

(3) The partial pressure of oxygen is always lower than that required to form Si_2N_2O as the mixture contains an excess of carbon ($1SiO_2:4C$). The excess carbon in the pellet acts as a substrate for Reaction 4 but some SiO also escapes un-nitrided and subsequently reacts on the graphite crucible walls.

The crystal shapes produced within the sample pellet are twisted and facetted as shown in Fig. 2a due to restricted growth within pores and cavities but when grown on a free surface such as the top of the pellet or the crucible walls, perfect whisker and needle growths are produced. Examples are shown in Fig. 3.

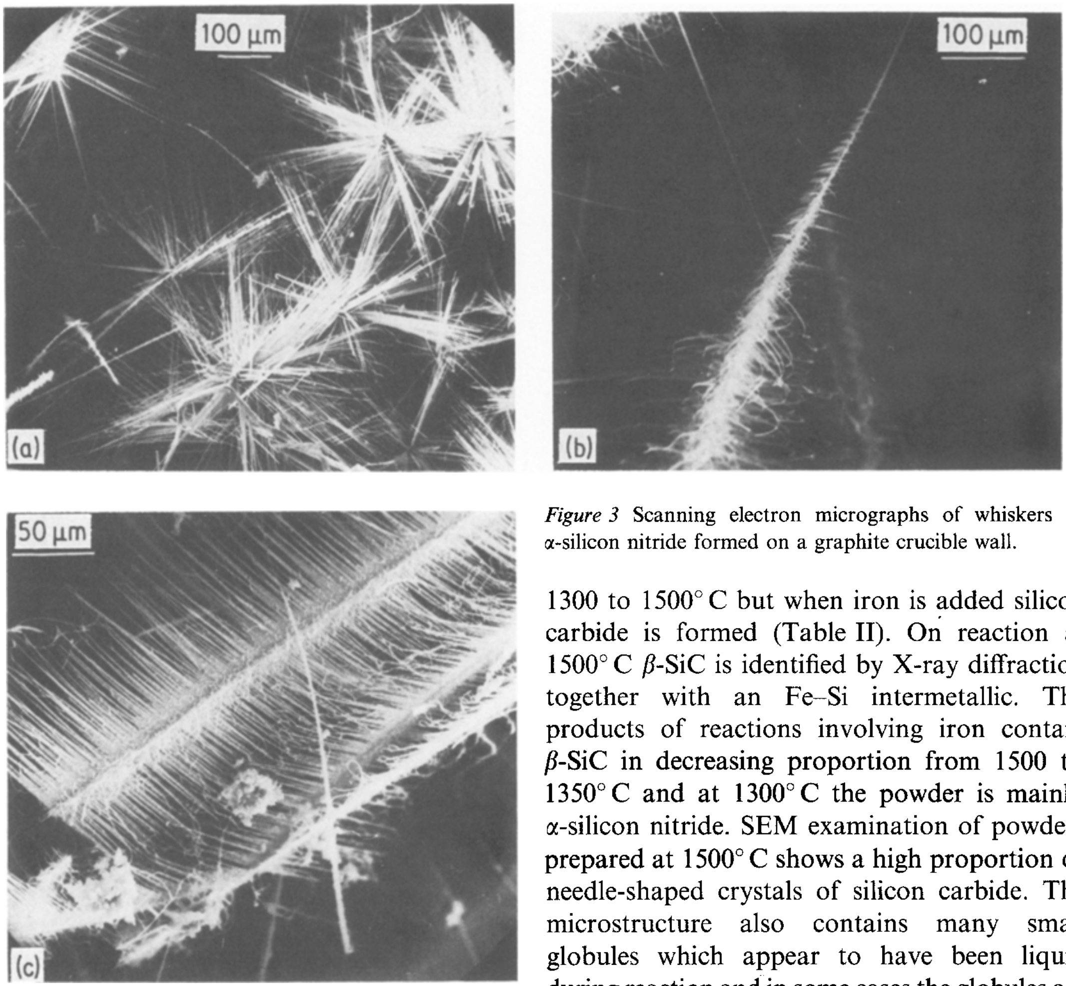

Figure 3 Scanning electron micrographs of whiskers of α-silicon nitride formed on a graphite crucible wall.

The results of the investigation of the effect on iron additions to $1SiO_2:4C$ mixes are shown in Table II. Pellets of $SiO_2:C$ powders produce pure α-silicon nitride which after grinding to powder has an equiaxed uniform grain size (Fig. 4). α is formed in the temperature range 1300 to 1500° C but when iron is added silicon carbide is formed (Table II). On reaction at 1500° C β-SiC is identified by X-ray diffraction together with an Fe–Si intermetallic. The products of reactions involving iron contain β-SiC in decreasing proportion from 1500 to 1350° C and at 1300° C the powder is mainly α-silicon nitride. SEM examination of powders prepared at 1500° C shows a high proportion of needle-shaped crystals of silicon carbide. The microstructure also contains many small globules which appear to have been liquid during reaction and in some cases the globules are seen to be attached to the ends of the needles. Fig. 5 shows an example and X-ray micro-analysis (Fig. 6) reveals that the globules have a high iron content. The globules also contain silicon and although the precise composition could not be obtained by microanalysis it is suggested that

TABLE II Results of nitriding $1SiO_2:4C$ powder mixtures with additions of iron

Temperature (° C)	Time (h)	Weight loss (%)	X-ray analysis (%)			
			α	β	SiC	Other
(a) *5 wt % iron*						
1500	19	62	–	–	100	tr. Fe–Si
1400	19	51	60	10	30	tr. Fe–Si
1350	19	50	70	10	20	tr. Fe–Si
1320	15	47	95	5	–	tr. Fe–Si
1300	19	47	95	5	–	tr. Fe–Si
(b) *2 wt % iron*						
1500	16.5	61	2	2	96	tr. Fe–Si
1400	16.0	52	30	20	50	tr. Fe–Si
1320	17.5	45	80	20	tr	tr. Fe–Si
1300	16.0	45	90	10	–	tr. Fe–Si

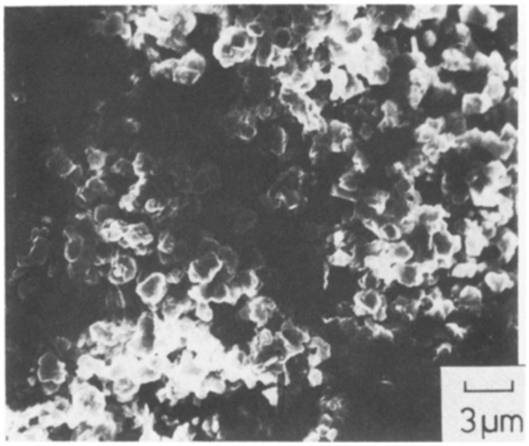

Figure 4 Scanning electron micrograph of α-silicon nitride prepared by carbothermal reduction and nitriding of silica (after Szweda *et al.* [1]).

these are the Fe–Si intermetallic phase identified by X-ray diffraction.

The iron–silicon phase diagram contains four eutectics at around 1250° C [15] and the formation of Fe–Si liquid phases at reaction temperature is therefore possible. A mechanism involving the presence of liquid metallic globules may be advanced to explain the formation of silicon carbide and the apparent decrease in stability of α-silicon nitride. It was shown above that reduction of SiO to silicon has a small negative free energy but if the silicon is at low activity then the reaction becomes thermodynamically favourable. The activity of silicon in liquid iron–silicon alloys is extremely low (Chart [15]) and thus in a strongly reducing environment the formation of Fe–Si liquid alloys is possible. In contact with excess carbon this liquid phase will also be saturated with carbon and thus the composition of the liquid in equilibrium with SiC and C may be calculated [16]. The liquid phase will act as (1) a sink for silicon (from SiO reduction) and carbon, and (2) a source of SiC precipitation. A continuous growth process therefore occurs by solution of the elements and precipitation of SiC. A similar process for growth of silicon nitride during nitriding of silicon containing iron impurities has also been proposed [17] and, as pointed out by Smith and White [10], in the presence of carbon, carbide rather than nitride precipitation is favoured. Reduction of SiO by carbon is enhanced when iron is present and the extent of nitriding of SiO to form α-silicon nitride is correspondingly reduced. The concentration of silicon in liquid iron in equilibrium with SiC and C [16] does not vary significantly with temperature and may be taken as 22 wt % Si which from the data of Chart [15], has a melting point around 1300° C. Below this temperature no liquid phase is present and so SiC will not form. This temperature is in reasonable agreement with the data shown in Table II.

The structure of SiC produced at 1500° C in $1SiO_2:4C$ samples containing iron was examined by TEM. Fig. 7a shows a bright-field micrograph of a needle of SiC which appears to

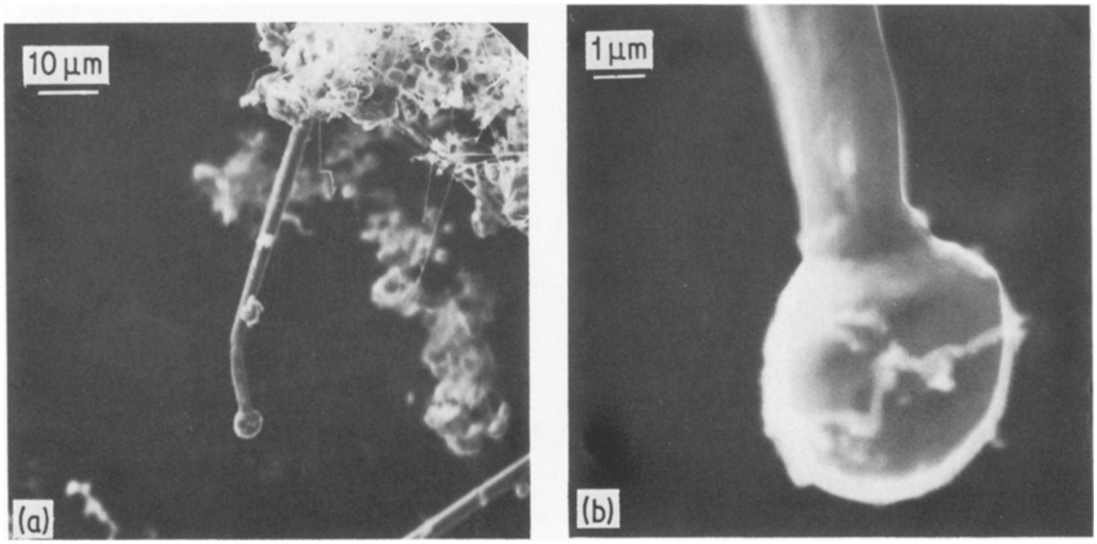

Figure 5 Scanning elecron micrograph of needles of SiC with globule formation on the end of a needle.

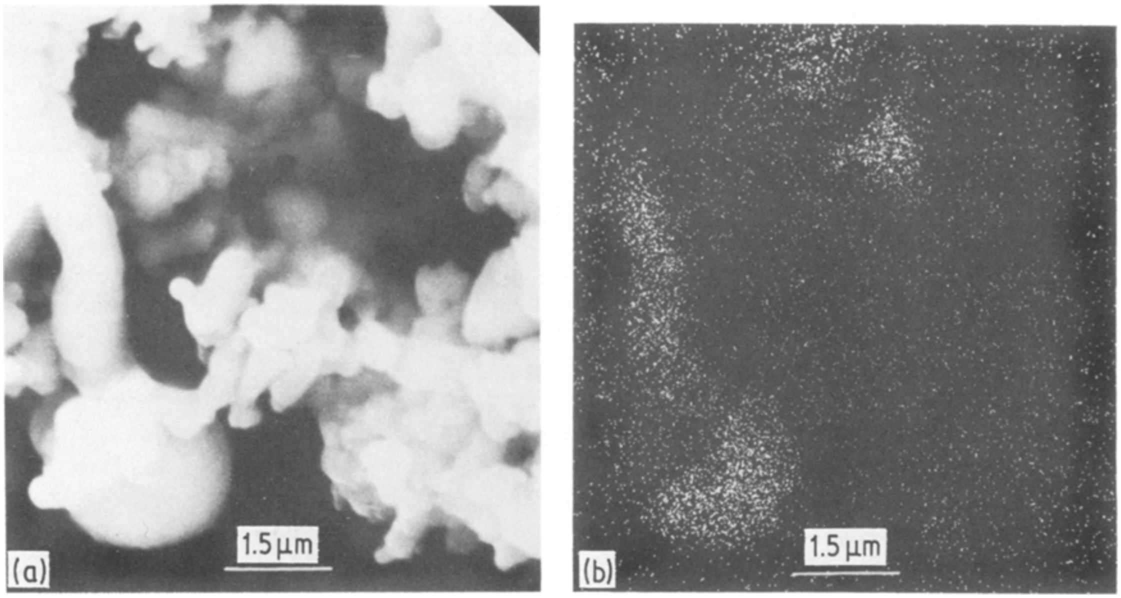

Figure 6 (a) Scanning electron micrograph of globules in a sample of $1SiO_2 : 4C$ with 5 wt % Fe addition nitrided at 1500° C. (b) Fe*Kα* X-ray map showing the concentration of iron in the globules.

have a coating on the surface. Dark-field imaging shows that this coating is amorphous and Fig. 7b shows an image from an SiC reflection in which the amorphous nature of the coating is obvious. This sample contains excess carbon after reaction and if this is removed by oxidizing the reacted powder in air at 700° C and the powder re-examined in TEM, then the needles of SiC are found to have no surface coating (Fig. 8). It is therefore concluded that the coating is amorphous carbon. The SiC needles grow from an Fe–Si liquid which is saturated in carbon and may therefore develop a carbon coating as they grow.

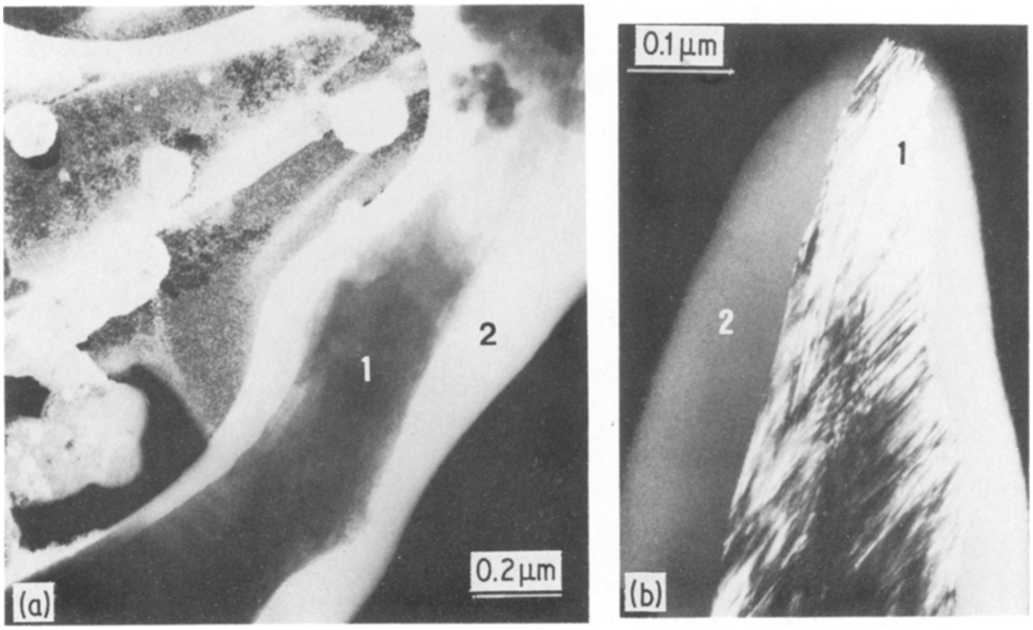

Figure 7 (a) Bright-field and (b) dark-field transmission electron micrographs of needles of SiC showing an amorphous surface layer. On each micrograph 1 indicates the crystalline needle and 2 the amorphous surface.

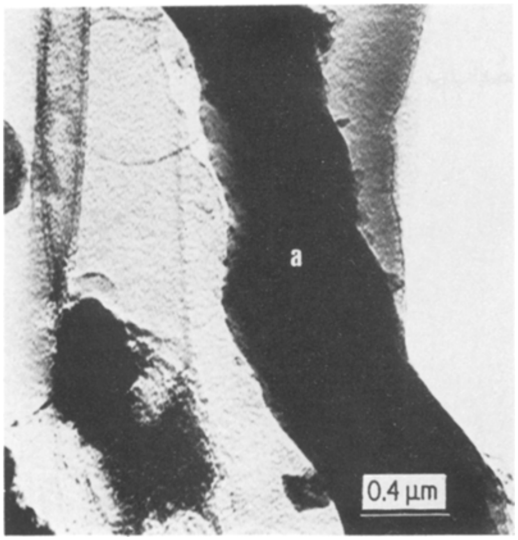

Figure 8 TEM bright-field micrograph of a needle of SiC after oxidation at 700° C in air. The SiC needle (a) has no surface layer.

5. Conclusions

The phases formed in the solid–gas system Si–C–O–N may be predicted from a knowledge of the free energies of formation of the phases at equilibrium. However, in the presence of impurity elements, liquid phases form which alter the phase equilibria by changing the thermodynamic activity of the phases and altering the rates of competing reactions. The effect of iron additions to $SiO_2:C$ powders is to promote SiC formation during nitriding at the expense of silicon nitride. Iron results in formation of pure SiC at 1500° C in a $SiO_2:C$ mixture which, when nitrided in the absence of iron, gives pure α-silicon nitride.

Carbothermal reduction and nitriding of silica is a practicable alternative to nitriding of silicon for production of silicon nitride but care must be taken to avoid impurities such as iron which may be present in the raw materials or introduced during processing. Two examples from the present work illustrate the point. (1) A 10 kg batch of high purity $1SiO_2:3C$ mixture was prepared by wet-milling and granulation in steel-lined equipment. Samples taken for chemical analysis contained 0.13 wt % Fe_2O_3 and on nitriding at 1450° C, the product consisted of 85% silicon nitride and 15% silicon carbide. (2) The ash produced by combustion of rice husks in a limited supply of air is essentially SiO_2 and carbon with trace impurities which are dictated by the soil in which the rice is grown. A sample of rice-husk ash containing 0.03 wt % Fe_2O_3 produced 85% silicon nitride and 15% silicon carbide on nitriding at 1450° C although it should be noted that several other trace impurity elements are present in this raw material.

Silicon carbide is an undesirable constituent of many engineering applications of silicon nitride and sialons produced from it, and it is clear therefore that while carbothermal reduction presents an attractive route for commercial production of silicon nitride, exclusion of iron from the raw materials is essential.

Appendix

(1)

$$2C + O_2 = 2CO \qquad (A1)$$

$$0.0133Si_{76}N_{100}O_2 + O_2 = 1.0133SiO_2 + 0.67N_2 \qquad (A2)$$

$$0.0566Si_{76}N_{100}O_2 + O_2 = 2.111Si_2N_2O + 0.67N_2 \qquad (A3)$$

$$1.33Si_3N_4 + O_2 = 2Si_2N_2O + 0.67N_2 \qquad (A4)$$

$$0.67Si_2N_2O + O_2 = 1.33SiO_2 + 0.67N_2 \qquad (A5)$$

$$25.33Si_3N_4 + O_2 = Si_{76}N_{100}O_2 + 0.67N_2 \qquad (A6)$$

$$SiC + 0.67N_2 = 0.33Si_3N_4 + C \qquad (A7)$$

$$4SiC + O_2 + 2N_2 = 2Si_2N_2O + 4C \qquad (A8)$$

$$1.33SiC + O_2 + 0.67N_2 = 0.67Si_2N_2O + 1.33CO \qquad (A9)$$

(2) The boundary lines in Fig. 1 are fitted to the following equations using the partial pressure data of Table I. The line numbers are given together with those of Smith and White [10] for ease of comparison.

Fig. 1	[10]	
1	8	$-53\,400 - 41.9T + 9.15T \times \log p_{CO}$

2	17	$-120\,413 - 7.84T + 3.065T \times \log p_{N_2}$
3	18	$+88\,618 - 146.17T + 3.065T \times \log p_{N_2}$
4	19	$-20\,595 - 80.43T + 3.065T \times \log p_{N_2}$
5	20	$-181\,231 + 34.20T + 3.065T \times \log p_{N_2}$
6	21	$-1\,832\,970 + 1060T + 3065T \times \log p_{N_2}$
7	24	The decomposition temperature of β in the presence of carbon is independent of p_{O_2} and may be calculated from $3.065T \log p_{N_2} = -46\,680 + 2.73T \log T + 17.8T$
8	25	$-206\,580 + 10.92 \log T - 9.8T - 9.15T \log p_{N_2}$
9	26	$-104\,984 + 3.63T \log T - 30.94T - 3.065T \log p_{N_2} + 6.08 \log p_{CO}$

Acknowledgements

The authors gratefully acknowledge the encouragement and support of Professor K. H. Jack FRS and other colleagues in the Wolfson Research Group of High-Strength Materials, Crystallography Laboratory. We also acknowledge the support of the British Council in providing a research studentship for S. A. Siddiqi.

References

1. A. SZWEDA, A. HENDRY and K. H. JACK, "Special Ceramics 7", Proceedings of the British Ceramic Society No. 31, edited by J. Taylor and P. Popper (British Ceramic Society, Stoke-on-Trent, 1981) p. 107.
2. A. HENDRY and K. H. JACK, "Special Ceramics 6", edited by P. Popper, (B.C.R.A., Stoke-on-Trent, 1975) p. 199.
3. K. KOMEYA and H. INOUE, *J. Mater. Sci.* **10** (1975) 1244.
4. J-G. LEE, PhD thesis, University of Utah (1976).
5. J-G. LEE and I. B. CUTLER, "Nitrogen Ceramics", edited by F. L. Riley (Noordhof, Leyden, 1977) p. 175.
6. S. C. SINGHAL, *Ceramurgia Int.* **2** (1976) 123.
7. A. HENDRY, "Nitrogen Ceramics", edited by F. L. Riley (Noordhof, Leyden, 1977) p. 183.
8. M. B. FEGLEY, *Comm. Amer. Ceram. Soc.* **64** (1981) C124.
9. O. KUBASCHEWSKI and C. B. ALCOCK, "Metallurgical Thermochemistry" (Pergamon Press, Oxford, 1979).
10. P. L. SMITH and J. WHITE, *Trans. J. Brit. Ceram. Soc.* **82** (1983) 23.
11. Y. K. RAO and H. G. LEE, *ibid.* **82** (1983) 123.
12. J. WEISS, H. L. LUKAS, J. LORENZ, G. PETZOW and H. KREIG, *Calphad* **5** (1981) 125.
13. I. COLQUHOUN, S. WILD, P. GRIEVESON and K. H. JACK, *Proc. Brit. Ceram. Soc.* **22** (1973) 207.
14. J. L. WOODHEAD, *Sci. Ceram.* **4** (1968) 105.
15. T. G. CHART, *High Temp. – High Press.* **2** (1970) 461.
16. H. REIN and J. CHIPMAN, *J. Phys. Chem.* **67** (1963) 839.
17. D. R. MESSIER and W. J. CROFT, "Preparation and Properties of Solid State Materials" Vol. 7, edited by W. R. Wilcox (Marcel Dekker, New York, 1982) p. 131.

Received 24 September
and accepted 16 October 1984