

Carbothermal Synthesis of Silicon Nitride: Effect of Reaction Conditions

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Conditions for carbothermal synthesis of α -Si₃N₄ are presented with special emphasis on the reaction temperature, C:SiO₂ ratio, and precursor mixing. With pure precursors, the conversion temperature is 1500° to 1550°C. An excess of C is necessary for complete conversion, and a simple sol-gelmixing technique provides excellent intermixing of the precursors. Copious flow of N2 gas throughout the reactor bed is essential if pure Si₃N₄ is to be produced; small concentrations of CO and O₂ promote SiC and Si₂N₂O, respectively. [Key words: silicon nitride, carbothermal reduction, synthesis, temperature, mixing.]

I. Introduction

THE increasing interest in silicon nitride (Si_3N_4) ceramics has lead to a demand for high-quality, low-cost powders. Unfortunately, high-quality, commercially available powders are very expensive, whereas lower-cost powders are of relatively poor quality.¹ A variety of synthesis techniques are being used and investigated, including direct nitridation;² imide processing;³ vapor, laser, and plasma synthesis;^{4,5} and carbothermal reduction.⁶⁻⁹ Among these methods, the carbothermal reduction process promises to produce high-quality powders at low cost. This is due to the availability of inexpensive, high-quality SiO₂ and C raw materials.

The overall reaction which occurs during carbothermal reduction to Si₃N₄ is

$$3SiO_2(s) + 6C(s) + 2N_2(g) \rightarrow Si_3N_4(s) + 6CO(g)$$
 (1)

This reaction is believed to proceed via a two step process:⁶⁻⁹

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g)$$
 (2)

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and

$$3\operatorname{SiO}(g) + 3\operatorname{C}(s) + 2\operatorname{N}_2(g) \to \operatorname{Si}_3\operatorname{N}_4(s) + 3\operatorname{CO}(g) \quad (3a)$$

$$\operatorname{SiO}_2(s) + \operatorname{CO}(g) \to \operatorname{SiO}(g) + \operatorname{CO}_2(g) \quad (3b)$$

and/or

$$3\text{SiO}(g) + 3\text{CO}(g) + 2\text{N}_2(g) \rightarrow \text{Si}_3\text{N}_4(s) + 3\text{CO}_2(g)$$

(4)

The CO₂ formed may be subsequently reduced to CO by any excess C.

The reaction sequences indicated are the most commonly acknowledged, but their acceptance is by no means universal.¹⁰⁻¹⁴ Barnitskaya et al.¹³ suggest that pure Si₃N₄ can only be formed if small additions of Fe are made to the raw materials, whereas Siddiqi and Hendry¹⁴ show that Fe promotes SiC formation over Si₃N₄.

Considerable disagreement exists in the literature over the reaction temperature range, with published values ranging from 1350° to 1550°C. $^{6-8,14-18}$ At higher temperatures, β -SiC is invariably found as the product. The difficulty in comparing results from different studies is compounded by the extreme sensitivity of the "optimum" temperature to the presence of impurities or additives, such as Fe and alkali elements. In general, all such impurities tend to lower the temperature range in which Si₃N₄ forms.

These discrepancies in the published literature lead to the present work. The objectives of this study are, therefore, to investigate the conditions for the carbothermal synthesis of Si_3N_4 with special emphasis on the reaction temperature, C:SiO₂ ratio, and the degree of intermixing of the raw materials (SiO₂ and C).

II. Experimental Procedure

High-purity carbon blacks and fumed silicas were used as the raw materials; their physical and chemical characteristics are listed in Table I. Weight losses due to volatiles were determined by heating them under the same conditions used for carbothermal reduction, outlined below.

The mixing of the SiO₂ and C powders was accomplished by either dry mixing or a sol-gel route. The former was con-

Table 1. Precursor Powder Characteristics*					
Grade	Surface area (m ² /g)	Impurity content (ppm)	Major impurity	Volatility (%)	Actual weight loss (%)
			Silica		
EH-5	380	38	Fe. Al. Na	2.5	5.1
M-5	200	38	(<5 ppm each)	2.0	4.2
LM130	130	38	(- FF,	1.0	3.9
			Carbon		
M1300	500	58	CN, Ni, Cr	9.5	17.7
M1000	343	38	(<10 ppm each)	9.5	
M880	220	15	(ito ppin each)	1.5	0.7
	210	10		15	5 7

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*Manufacturer's specifications (Cabot Corp., Boyertown, PA), except for the actual weight losses, which were measured after heating at 1500°C in N2

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ducted in a dry plastic wash-bottle with 10-mm alumina media using vigorous agitation for 10 to 15 min. Precursors were blended for 15 min in a laboratory blender with isopropyl alcohol (reagent grade). The ratio of SiO₂ to isopropyl alcohol was kept constant at 15 g/500 mL so that the sol did not become too viscous. After blending, the sol was dried until a friable gel remained. The course granules of the gel were then ground to a loose powder, using either a pestle and mortar or a blender (the latter for a few seconds). The two resulting powders were quite different from each other: the blended powder was much finer and free flowing compared with the hand-ground powder. The latter had soft agglomerated lumps due to the compacting nature of grinding with a pestle and mortar and, therefore, had the greater tap density of the two.

All nitriding experiments were conducted in an inertatmosphere, vertical-tube furnace, the inner diameter being 63.5 mm, with a hot zone of 100 mm.¹⁹ The gas used was highpurity N₂ gas which was maintained at a constant linear flow



(a)

rate of 31 cm/min. The N2 gas was also purged of O2 gas prior to nitriding, by passing the gas through a Ti sponge getter at a temperature of 800°C. To prevent the back diffusion of air from the gas outlet into the furnace, the exhaust gas exited through a gas bubbler filled with rotary-vacuum-pump oil. The furnace was maintained at atmospheric pressure.

To eliminate O_2 from the system before nitriding, the furnace was flushed three times with N_2 using a rotary vacuum pump. Once the flushing was complete, the crucible containing the reactants was slowly raised over a period of 20 min into the hot zone of the furnace.

The crucibles were made of either high-purity alumina[†] or graphite.[‡] The base of the graphite crucible was perforated with holes (\sim 3 mm in diameter), which allowed the gas to flow freely through the reactants. The precursor materials

[†]Coors, Golden, CO. [‡]Grade 3455, Speer, Montreal, Canada.



(b)



(c)



(d)

Fig. 1. SEM micrographs of powder morphology as a function of reaction temperature: (a) 1350°, (b) 1500°, (c) 1550°, and (d) 1600°C.

were prevented from falling out of the crucible by a thin layer of graphite felt over the base.

The reacted material was finally heated in air at 800°C for 1 to 2 h until all the C was volatilized as gaseous CO or CO₂. The product was analyzed by X-ray diffraction to determine the phases present as well as their amounts. Integrated peak areas were used to determine the relative amounts, using standard procedures.²⁰ The peak areas were manually integrated using an image analyzer.[§] Analysis was straightforward since a maximum of only two crystalline phases was observed at any time; low-reaction-temperature products had an amorphous SiO₂ peak as well. The area of large, sharp peaks could be accurately determined (±1%), whereas greater uncertainty was associated with amorphous and small peaks (±10%). These uncertainties, however, do not affect the conclusions of this study.

III. Results and Discussion

(1) Reaction Temperature

The reaction products formed were very sensitive to the reaction temperature.¹⁹ The effect of the reaction temperature was investigated using a sol-gel-derived precursor with a C:SiO₂ molar ratio of 7:1. The reaction was conducted for 5 h at temperature with the precursor placed in a graphite crucible. The effect of precursor preparation, C:SiO₂ ratio, and crucible type are described later. A reaction time of 5 h was selected since preliminary investigations indicated that the reaction was completed in ≤ 4 h. At reaction temperatures of <1500°C, only partial conversion to α -Si₃N₄ occurred, the remainder being unconverted SiO₂ and/or Si₂N₂O. For example, at 1450°C, only 20 wt% α -Si₃N₄ was produced. Complete conversion occurred over the narrow temperature range of 1500° to 1550°C; at higher temperatures, β -SiC was produced. At 1600°C, 79 wt% β -SiC was formed.

The morphology of the reaction products is also influenced by the reaction temperature (Figs. 1(a) to (d)). At low temperatures (<1500°C), unreacted SiO₂ is present throughout. At 1500° to 1550°C, discrete particles of α -Si₃N₄ are observed with a mean particle size of ~ 2.5 to 3 μ m. At higher temperatures, the structure becomes less uniform and is associated with β -SiC formation. The raw materials used in this study were very pure, and free of Fe and alkalis. Thus, the range of 1500° to 1550°C represents the highest range over which α -Si₃N₄ can be formed by carbothermal reduction; higher temperatures promote β -SiC formation. Impurities, individually and synergistically, would reduce the range to lower temperatures. The presence of impurities is likely to be one possible reason for the lower temperature ranges reported in the literature.^{6-8,14,16-18} Unfortunately, these impurities tend to be retained in the final product, with undesirable consequences with respect to the high-temperature mechanical properties of Si₃N₄ ceramics.

Another reason for a shift in the formation temperature may be due to the composition of the gas. Our studies²¹ indicate that small amounts of O₂ and CO can significantly affect the solid products formed, as illustrated in Fig. 2. This predominance diagram was generated by calculating the O₂ and CO partial-pressure regions over which the different solid phases are stable. The data in Fig. 2 were calculated for a reaction temperature of 1500°C and a constant N₂ pressure of 0.98×10^5 Pa. It shows that, at O₂ partial pressures in excess of 7.2×10^{-15} Pa, Si₂N₂O is the stable equilibrium phase. Similarly, at CO partial pressures above ~3.5 Pa, β -SiC is the stable phase. High CO partial pressures have also been reported to promote β -SiC formation during the carbothermal reduction of kaolinite to β' -sialon.²² The partial pressure of O₂ can easily be maintained below this critical value by get-



Fig. 2. Predominance diagram for the Si-O-N-C system calculated for 1500°C.

tering the N₂ gas over a heated Ti sponge. Control of CO is more difficult, since it is a reaction product. However, its level can be kept low only by having a copious flow of N₂ throughout the reactor bed. Localized low-flow regions must not be allowed to occur if β -SiC formation is to be avoided.

(2) C:SiO₂ Ratio

According to Eq. (1), the stoichiometric molar ratio of C:SiO₂ is 2:1. In practice, the amount of C required is generally greater than this. The influence of the C:SiO₂ ratio on the extent of the α -Si₃N₄ formation is demonstrated in Fig. 3. The reaction was conducted using a sol-gel-derived precursor at 1500°C for 5 h in N₂ gas flowing at a linear rate of 31 cm/min.

The data obtained using the graphite crucible show that a $C:SiO_2$ ratio in excess of 4:1 is required before full conversion occurs. It is not unexpected that excess C is required. If the carbothermal process follows the two-stage reaction route (Eqs. (2) to (4)), then physical contact between C and SiO_2 is essential for SiO-gas formation. Full conversion using a stoichiometric ratio of $SiO_2:C$ (1:2) can occur only if there is perfect contact between C and SiO_2 particles (an unlikely



Fig. 3. Effect of C:SiO₂ molar ratio on the extent of conversion at 1500° C.

[§]Model IBAS, Zeiss, Thornwood, NY.

situation). The other step in the conversion of SiO_2 to Si_3N_4 can be via gas-solid and/or gas-gas reactions, Eqs. (3a) and (4), respectively. In the absence of seeding, Si_3N_4 will first form on a C site via a gas-solid reaction. Subsequently, the gas-gas reaction may also occur. 15,24,25 The presence of excess C can aid both processes by acting as a site for Si₃N₄ formation, and by reducing the CO_2 formed (in Eq. (4)) to CO. This CO can then promote Eq. (4). Hence, a small excess of C may be beneficial to the carbothermal synthesis process. Note that the excess C must be kept to a minimum to minimize the time-temperature cycle needed for decarburization. Extended exposure to the decarburization temperature can result in the final powder having a high-O₂ content. The amount of excess C required for full conversion depends on the extent of intermixing. Better intermixing would require a smaller excess than poorly mixed raw materials. Also, highersurface-area particles should also permit better intermixing. These two aspects are dealt with in more detail later.



(a)

The amount of C affects the morphology as well (Figs. 4(a) to (d)). At low C contents, unreacted SiO₂ remains, whereas, at C:SiO₂ values in excess of 7:1, discrete particles form, that, in some instances, appear hexagonal in shape. The shape and size of these Si₃N₄ particles are not significantly affected by the amount of excess C. They are, however, sensitive to precursor preparation methods and by the presence of seed crystals.^{15,19,25}

Note that the alumina crucible did not contain holes in its base. Therefore, N_2 gas flowed around and over but not through the crucible. The use of such a crucible is likely to have two consequences. First, the concentration of the gaseous reaction products will be significantly larger within the crucible. This would tend to alter the equilibrium conditions for Eqs. (1) to (4), thereby hindering the conversion process. This can be determined by measuring the weight loss in both crucibles as a function of C:SiO₂ ratio. It is assumed that the SiO₂ weight loss (as SiO gas) would increase with the



(b)



(c)

(d)

Fig. 4. SEM micrographs of powder morphology as a function of $C:SiO_2$ ratio (sol-gel powder, 1500°C reaction temperature, graphite crucible): (a) 2:1, (b) 4:1, (c) 7:1, and (d) 10:1.

rate of SiO formation, a reasonable assumption. Figure 5 shows that, for the alumina crucible, the weight loss increases to a maximum of $\sim 20\%$ at 4:1 before slowly decreasing to $\sim 10\%$ at 10:1. In comparison, the loss from a graphite crucible is $\sim 34\%$ at 2:1 before falling more rapidly to $\sim 10\%$ at $\geq 7:1$. These weight losses were determined after subtracting the losses associated with volatiles and that due to CO production by the reactions.

The ability of N_2 gas to flow through the graphite crucible allows rapid removal of the product gases, such as CO. Hence, the reaction (Eq. (2)) does not slow down and the weight loss at C:SiO₂ of 2:1 is higher than that from the alumina crucible, where the gaseous product concentrations would have increased sufficiently to slow down the reaction. At higher C:SiO₂ ratios, the weight loss from the graphite crucible reaches its lowest level of 10% much faster. This is a consequence of the faster formation of Si₃N₄ because of the abundance of N₂ gas in the reactor bed.

The influence of the crucible on the final products, by affecting the local gas composition, is also shown by the formation of minor phases. With the graphite crucible, no secondary phases are observed under optimum conditions. With the alumina crucible, traces of β -SiC and Si₂N₂O are frequently found. An increase in the partial pressure of CO would account for β -SiC formation instead of Si₃N₄. In addition, increased O₂ and SiO partial pressures would promote Si₂N₂O formation. The presence of only small amounts of SiC and Si₂N₂O suggest that there are localized regions in the reactor bed with high partial pressures of CO and/or O₂/SiO. Since N₂ gas is able to flow through the perforated graphite crucible, such localized regions are less likely to occur unless the reactor bed is relatively impervious to gas flow.

The use of an alumina crucible can also result in a high partial pressure of O_2 via

$$\operatorname{Al}_2\operatorname{O}_3(s) \to \operatorname{Al}_2\operatorname{O}_2(g) + \tfrac{1}{2}\operatorname{O}_2(g) \tag{5}$$

The partial pressure of O_2 generated by this reaction $(\sim 10^{-12} \text{ Pa})$ is significantly higher than that required to form $\text{Si}_2\text{N}_2\text{O}$ at 1500°C. The presence of gaseous aluminum suboxides has also been suggested elsewhere.²³ Thus, the use of an alumina crucible is undesirable if Si_3N_4 is the reaction product sought.



Fig. 5. SiO₂ weight loss as SiO gas as a function of $C:SiO_2$ ratio at 1500°C.

(3) Precursor Preparation

The preceding results illustrate the significant impact of the precursor on the reaction kinetics. These results are confirmed by the data plotted in Fig. 6. The extent of conversion using sol-gel and dry-mixed raw materials is plotted versus the C:SiO₂ ratio. Both materials were used in the powdered form (<425 μ m), spread in a thin layer over graphite felt. The sol-gel powder achieved complete conversion at >4:1, whereas the dry-mixed powder failed to achieve >35% Si₃N₄ even with a C:SiO₂ ratio of 10:1. This illustrates the importance of having excellent intermixing between C and SiO_2 . Better intermixing was achieved with the sol-gel process. The sol-gel-processing route was also found to be easily reproducible. We compared our data with that of Szweda et al.,6 who arrived at different conclusions. They found that drymixed powders proved better at achieving full conversion. They suggested that excess C is required with sol-gelprocessed powder to counteract the effect of the high moisture content, which is believed to increase the O_2 partial pressure and promote Si_2N_2O . The results presented here are for sol-gel-processed powders using isopropyl alcohol. However, data obtained using water gave identical results, provided a drying step of 10 h at 300°C in air was incorporated prior to carbothermal reduction to completely eliminate all moisture. The reasons for the different results obtained with the drymixed powder are not clear. Unfortunately, insufficient information is available on the exact method adopted by Szweda et al.⁶ However, all the results suggest that the important factor is the degree of intermixing achieved. Therefore, any means of providing good intermixing should be a viable method given that impurities (H₂O, etc.) are not present.

There is another property that the precursor must possess: N_2 gas must be allowed to flow easily throughout the reactants. The importance of this is demonstrated in Fig. 7. Note that even the well-mixed, sol-gel-processed material, when pelletized by die pressing at 70 MPa, will not completely convert unless gas is able to freely permeate the reactants, as is the case in the loose state. Full conversion is never achieved with pelletized or dry-mixed precursors. The importance of N_2 -gas flow is also demonstrated by the selective formation of Si_3N_4 in the pellets.¹⁵ Si_3N_4 formation occurs only on the surface and in cracks in the pellets, i.e., in areas easily accessible to N_2 gas.

(4) Effect of C and SiO₂ Surface Areas

One possible method by which good intermixing can be achieved is by using high-surface-area raw materials. The



Fig. 6. Effect of the precursor preparation method on extent of conversion at 1500°C.



Fig. 7. Effect of precursor form on the extent of conversion at 1500° C.

properties of the raw materials listed in Table I show that all the carbon blacks and silicas have surface areas much larger than the surface area of the Si₃N₄ produced ($\sim 2 \text{ m}^2/\text{g}$). Therefore, they should all prove equally satisfactory. This, however, is not the case, as shown by the results plotted in Figs. 8 and 9. As the surface area of the C increases, the extent of conversion to α -Si₃N₄ increases, with only the highest-surface-area C proving satisfactory. The data again demonstrate the need for an open precursor structure to allow easy N_2 -gas flow through the reactants. The influence of SiO₂ surface area is, however, small (Fig. 9). There is no significant change in the extent of conversion of SiO_2 to Si_3N_4 with the size of SiO₂ particles. This suggests that even the coarsest particle size $(125 \text{ m}^2/\text{g})$ is sufficient for good mixing. In the past,¹⁰ SiO₂ particles of very much lower surface area (0.01 to $2 \text{ m}^2/\text{g}$ have been observed to influence the extent of conversion. Thus the reaction kinetics are more affected by comparatively large particles than by ultrafine silicas.



Fig. 8. Effect of the C surface area on the extent of conversion at 1500°C with 7:1 sol-gel-powder precursor (loose powder and pellets).



Fig. 9. Effect of SiO_2 surface area on the extent of conversion at $1500^{\circ}C$ with 7:1 sol-gel-prepared loose-powder precursor.

The significance of the C surface area may be a consequence of the need to ensure that the SiO_2 particles remain separated to avoid sintering, as well as to ensure physical contact with SiO_2 . The latter is necessary for the first reaction (Eq. (2)) to occur. Similar conclusions were arrived at by Zhang and Cannon⁷ using lamp black, pyrolyzed starch, and organically precipitated silicas. Note that more aggressive mixing methods, such as attrition milling, may enhance the degree of intermixing and permit the use of coarser raw materials and lower C contents. These aspects are presently being investigated.

IV. Summary

The results of this study demonstrate the importance of the processing conditions during the carbothermal synthesis of silicon nitride (Si_3N_4) .

(1) With pure precursor materials, complete conversion to α -Si₃N₄ occurs over the narrow temperature range of 1500° to 1550°C.

(2) An excess of C is required for full transformation.

(3) The sol-gel-processing route allows for good, reproducible intermixing of precursor SiO_2 and carbon black.

(4) Increasing the C surface area increases the extent of conversion to α -Si₃N₄. In contrast, changing the SiO₂ surface area (100 to 400 m²/g) has no significant effect on the extent of conversion.

(5) Copious flow of N₂ gas throughout the reactor bed is essential. This ensures adequate N₂ for the conversion to Si₃N₄ and prevents the formation of β -SiC or Si₂N₂O by reducing the partial pressure of the other gaseous species.

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