

# The Chemistry of the Carbothermal Synthesis of $\alpha$ - $\text{Si}_3\text{N}_4$ : Reaction Mechanism, Reaction Rate and Properties of the Product

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## Abstract

*It is believed that the reaction mechanism of the formation of  $\text{Si}_3\text{N}_4$  from silica, carbon and nitrogen is still not clear. The assumption of solid-state diffusion as reaction mechanism resulted in success. A high value for the activation energy (420 kJ/mol) is obtained for this reaction. This high value probably indicates that the reaction rate is determined by the diffusion of C atoms in carbon. Grain growth of  $\text{Si}_3\text{N}_4$  is limited to smaller grains. Due to incorporation of oxygen in the crystal lattice, the  $\text{Si}_3\text{N}_4$  powder as produced contains about 1.5 wt% oxygen. An excellent  $\alpha$ - $\text{Si}_3\text{N}_4$  powder can be obtained by the carbothermal synthesis.*

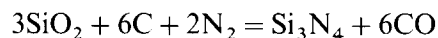
*Der Reaktionsmechanismus, der zur Bildung von  $\text{Si}_3\text{N}_4$  aus Siliziumdioxid, Kohlenstoff und Stickstoff führt, scheint noch nicht vollständig geklärt zu sein. Die Annahme, daß Festkörperdiffusion den Reaktionsmechanismus darstellt führte zum Erfolg. Es wird eine hohe Aktivierungsenergie (420 kJ/mol) für diese Reaktion beobachtet. Dieser hohe Wert weist wahrscheinlich darauf hin, daß die Reaktionsgeschwindigkeit durch die Diffusion von C-Atomen in Kohlenstoff bestimmt wird. Das Kornwachstum von  $\text{Si}_3\text{N}_4$  bleibt auf kleine Körner begrenzt. Infolge der Sauerstoffaufnahme im Kristallgitter, enthält das hergestellte  $\text{Si}_3\text{N}_4$ -Pulver etwa 1.5 Gew.% Sauerstoff. Mittels der carbothermischen Synthese kann  $\alpha$ - $\text{Si}_3\text{N}_4$ -Pulver mit hervorragenden Eigenschaften erzeugt werden.*

*Le mécanisme de l'élaboration de  $\text{Si}_3\text{N}_4$  à partir de*

*silice, carbone et nitrogène reste toujours confus. Cependant, si l'on suppose que ce mécanisme est régi par la diffusion dans une phase solide, on obtient alors des résultats prometteurs. Une forte énergie d'activation (420 kJ/mol) est produite pour cette réaction. Cette valeur indique probablement que la vitesse de réaction est déterminée par la diffusion des atomes C dans le carbone. Le grossissement des grains de  $\text{Si}_3\text{N}_4$  est limité aux plus petits. Dû à l'incorporation d'oxygène dans le réseau cristallin, la poudre de  $\text{Si}_3\text{N}_4$  produite contient environ 1.5% en poids d'oxygène. Une excellente poudre de  $\alpha$ - $\text{Si}_3\text{N}_4$  peut être obtenue par cette synthèse carbothermique.*

## 1 Introduction

Carbothermal synthesis of  $\text{Si}_3\text{N}_4$  is a relatively old process. It was developed in the late 19th–early 20th century by H. Mehnert and the well known C. Bosch.<sup>1,2</sup> The overall reaction can be described as



In those days research on silicon nitride was driven by the search for nitrogen fertilisers. In the second half of this century research on silicon nitride was driven by its use as a structural material. At first attention was focused on reaction-bonded silicon nitride and in the 1970s the (pressureless) sintering of  $\text{Si}_3\text{N}_4$  was discovered, in which submicron silicon nitride powder is sintered using additives which form a liquid phase with the surface silica at elevated temperatures.<sup>3</sup> A bright future was seen for products made from sintered  $\text{Si}_3\text{N}_4$  and for its raw material:

submicron silicon nitride powder. An extensive search started for the best way of making pure submicron  $\text{Si}_3\text{N}_4$  powder.

One of many processes for making submicron  $\text{Si}_3\text{N}_4$  powder is the carbothermal synthesis. This process is more complex from the chemical point of view than, for instance, the nitridation of silicon powder. Sintered silicon nitride with bend strengths of about 1000 MPa can be obtained by using carbothermally synthesised  $\text{Si}_3\text{N}_4$  powders.<sup>4-6</sup> The presence of some SiC is considered to be advantageous in order to obtain a high strength material. Many articles have been written about this process since the early 1970s, in which different types of  $\text{SiO}_2$  and C, different  $\text{SiO}_2$ :C ratios, different ways of mixing the  $\text{SiO}_2$  and C, and different nitrogen sources like  $\text{N}_2$ ,  $\text{N}_2$  plus  $\text{H}_2$  or  $\text{NH}_3$ , seeds and catalysts have been used.<sup>7,8</sup> Often the  $\text{SiO}_2$ -C mixtures are granulated prior to reaction. The reaction is usually followed by removal of free carbon with air at 650°C.

Typical features of the carbothermal synthesis of  $\text{Si}_3\text{N}_4$  are: a submicron powder is obtained; above a synthesis temperature of about 1500°C the product contains SiC, and this boundary temperature is influenced by impurities and catalysts like Fe;<sup>9</sup> seeds decrease the average particle size and increase the reaction rate;<sup>7</sup> catalysts like MgO are left in the product and act as sintering aid; SiO is observed but no free silicon; a product free of whiskers can be synthesised, and usually  $\alpha$ - $\text{Si}_3\text{N}_4$  is obtained. The most accepted reaction mechanism is:  $\text{SiO}_2 + \text{C} = \text{SiO} + \text{CO}$  and  $3\text{SiO} + 3\text{C} + 2\text{N}_2 = \text{Si}_3\text{N}_4 + 3\text{CO}$ . Reaction mechanisms including  $\text{CO}_2$  are reported as well in the literature.<sup>10</sup> The use of  $\text{NH}_3$  or a mixture of  $\text{N}_2$  and  $\text{H}_2$  leads to the formation of HCN<sup>4,11</sup> and therefore is of less interest for commercial production.

Due to all these differences in raw materials, processing and reaction conditions, many hypotheses concerning particle size of  $\text{Si}_3\text{N}_4$ , reaction mechanism and values for the activation energy of the reaction rate are found in the literature. Relations between reaction rate, reaction mechanism, particle size and other properties of the product are rare.

It is the aim of the authors to design a process for the carbothermal synthesis of  $\text{Si}_3\text{N}_4$  based on the following four characteristics:

- the use of relatively cheap raw materials;
- the use of pure raw materials or a suitable catalyst in order to avoid purification afterwards;

- the production of submicron powder without milling the  $\text{Si}_3\text{N}_4$ ; and
- the use of small excess of carbon powder in order to obtain 100% conversion of the  $\text{SiO}_2$ , removing the free carbon with a gasification reaction.

If this is achieved the process will be very competitive with other processes for the production of submicron silicon nitride powder, both in product quality and economic aspects. Such other processes are the nitridation of silicon powder, including acid leaching, or the synthesis from  $\text{SiCl}_4$  and  $\text{NH}_3$ , including the production of large quantities of  $\text{NH}_4\text{Cl}$ . In this paper evidence is presented that, in the present case, the minimum amount of oxygen in the product is about 1.5 wt% due to incorporation of oxygen in the crystal lattice, the minimum specific surface area of the product is about 5 m<sup>2</sup>/g due to the absence of grain growth for coarser particles, that the reaction mechanism is not yet clear, that the activation energy of the synthesis is 420 kJ/mol, and that this is probably related to solid-state diffusion of carbon atoms in carbon black.

## 2 Pre-synthesis Processing

In the authors' view the most interesting commercial  $\text{SiO}_2$  raw materials are milled quartz sand and fumed silica. Milled quartz sand is cheap, pure (less than 500 ppm of metallic impurities) but not reactive. The reactivity can be increased by using seeds and/or a catalyst. Fumed silica is pure (less than 300 ppm of metallic impurities), reactive but expensive. Milled petroleum cokes and carbon black, especially gas black, are considered as the most interesting carbon raw materials. Milled petroleum cokes are cheap, not very reactive and they contain usually less than 5000 ppm of metallic impurities. Gas black is reactive, pure and sometimes moderately priced. It usually contains less than 300 ppm of metallic impurities. Experiments were carried out with gas black (Printex U, Frankfurt, Germany) and a fumed silica (Aerosil OX 50). The gas black, silica and  $\text{Si}_3\text{N}_4$  powder were mixed in demineralised water using an attritor coated with polyurethane. The scale of mixing was 4 microns. PVA (3 wt%) was added. The molar ratio of  $\text{SiO}_2$ :C was 1:2 to 1:3, depending on the set of experiments.  $\text{Si}_3\text{N}_4$  powder (5 wt% relative to the silica) was added to act as nuclei. The  $\text{Si}_3\text{N}_4$  powder was LC-12 (H. C. Starck, Berlin, Germany). After mixing the slurry was either filtered, dried, the filter cake broken

into particles with a diameter less than 1 mm and tableted into tablets with a diameter of 5 mm, a height of 5 mm and a bulk density of  $1 \text{ g/cm}^3$  or dried and broken into particles with a diameter of less than 0.5 mm.

### 3 Experimental

The experiments to study the reaction mechanism were performed in a Carbolite horizontal tube furnace. Particles (10 g) with a diameter of less than 0.5 mm and a  $\text{SiO}_2:\text{C}$  molar ratio of 1:2.5 were poured into a boat of recrystallised SiC and placed in the sintered alumina tube with an inner diameter of 50 mm. The tube was flushed with a nitrogen flow of 20 g/h. Volatile matter was removed at temperatures up to  $1000^\circ\text{C}$ . The heating rate up to the reaction temperature of  $1470^\circ\text{C}$  was  $400^\circ\text{C/h}$ . After reaction and cooling the samples were studied with XRD, ESCA and TEM. The oxygen and nitrogen content were determined with LECO equipment, using the inert fusion method. The kinetic experiments were performed in a Netzsch STA 429 thermobalance at DSM Research (Geleen, The Netherlands). As samples the tablets with a molar ratio  $\text{SiO}_2:\text{C} = 1:2$  or  $1:3$  were used. The samples were placed on an alumina plate covered with graphite foil. The heating and cooling rate were each

$20^\circ\text{C/min}$ . A W versus W/Rh thermocouple was used in the thermobalance for temperature measurements. Nitrogen with less than 10 ppm impurities was used for the synthesis of  $\text{Si}_3\text{N}_4$ . As variables the gas flow rate, the number of tablets, the temperature, the size of the tablet and the  $\text{SiO}_2:\text{C}$  ratio were studied. The experiments to study grain growth were performed in a graphite furnace. The nitrogen flow through the furnace was almost stagnant. Samples of 10 g were heated in recrystallised SiC crucibles for 1 or 10 h at 1400, 1500 or  $1600^\circ\text{C}$ . The heating and cooling rates were  $10^\circ\text{C/min}$ . After the experiments the samples were analysed with SEM, the oxygen content was determined with LECO equipment and the specific surface area was measured according to the BET method. Data from the literature concerning grain growth of  $\text{Si}_3\text{N}_4$  powder was analysed as well.

### 4 Results

Table 1 gives the results of the experiments concerning the reaction mechanism: O and N content, conversion, ESCA and XRD. TEM was used to study the reaction mechanism as well. The  $\text{SiO}_2:\text{C}$  molar ratio was 1:2.5. Figure 1 shows the composition of the starting mixture: spherical carbon black particles with a diameter of 35 nm,

**Table 1a.** Results of experiments at  $1470^\circ\text{C}$  in  $\text{N}_2$  concerning the reaction mechanism

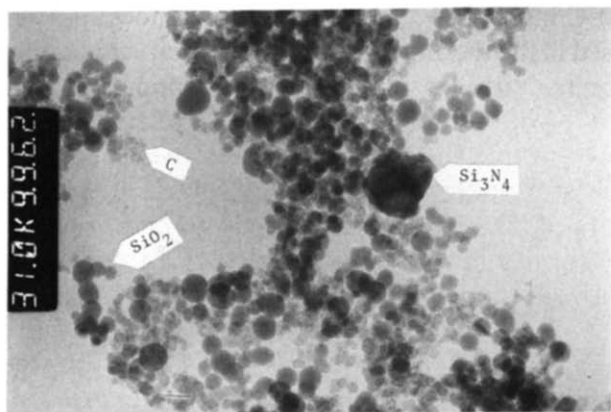
Number	Time (h)	O content (wt%)	N content (wt%)	Conversion (%)	XRD
0 <sup>a</sup>	—	38.2	1.0	0	$\alpha$ - $\text{Si}_3\text{N}_4$
1	0	35.5	2.6	6	$\alpha$ - $\text{Si}_3\text{N}_4$
2	1	28.6	8.9	30	$\alpha$ - $\text{Si}_3\text{N}_4$
3	2	19.9	15.8	55	$\alpha$ - $\text{Si}_3\text{N}_4$
4	4	2.7	31.7	97	$\alpha$ - $\text{Si}_3\text{N}_4$
5	6	1.7	32.0	98.5	$\alpha$ - $\text{Si}_3\text{N}_4$

<sup>a</sup> Raw material.

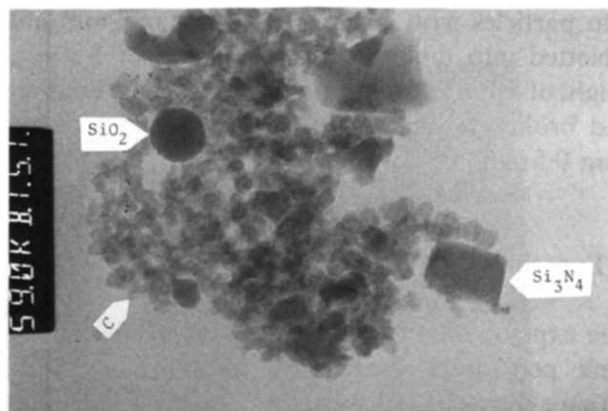
**Table 1b.** Results of experiments at  $1470^\circ\text{C}$  in  $\text{N}_2$  concerning the reaction mechanism

Number	Conversion (%)	Atomic ratio			
		O/Si	N/Si	C/Si	SiC/Si
		529, 532	397.5	283, 285, 289	289 (eV)
0 <sup>a</sup>	0	1.48	0.07	2.38	0.00
1	6	1.14	0.28	3.60	0.28
2	30	0.73	0.42	4.20	0.13
3	55	0.43	0.63	2.30	0.00
4	97	0.22	0.81	1.35	0.12
5	98.5	0.20	0.92	1.69	0.14

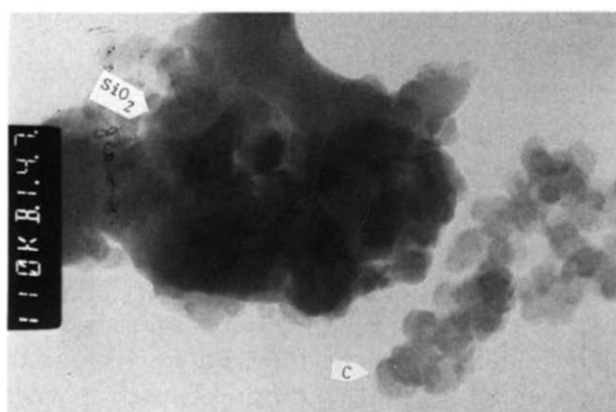
<sup>a</sup> Raw material.



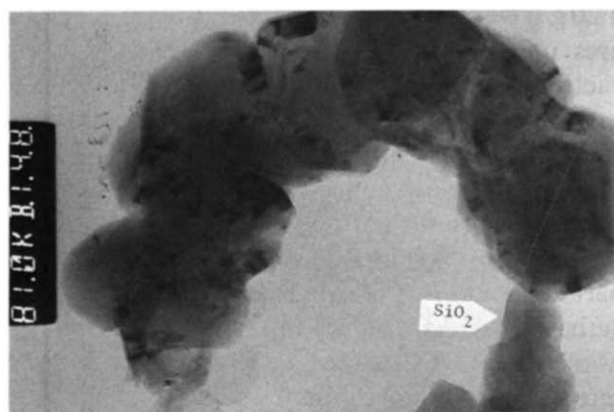
**Fig. 1.** Mixture of raw materials. The length of the black bar is 1600 nm. The large particle is  $\text{Si}_3\text{N}_4$ , the 160 nm diameter particles are silica and the 35 nm diameter particles are gas black.



**Fig. 3.** The mixture at 30% conversion. The length of the black bar is 850 nm. Silica, gas black and  $\text{Si}_3\text{N}_4$  particles are seen.



**Fig. 2.** The mixture at 6% conversion. The length of the black bar is 450 nm. The gas black particles have a diameter of 35 nm and a sintered silica agglomerate can be observed.



**Fig. 4.** The mixture at 30% conversion. The length of the black bar is 620 nm. Partially crystallised particles and amorphous silica can be seen.

spherical amorphous silica particles with a diameter of 160 nm and a silicon nitride seed. Figure 2 shows the mixture at 6% conversion. It can be seen that the silica agglomerates are partially sintered, with a diameter of the sintered agglomerate of about 500 nm. The carbon black particles have not changed in size: their diameter is still 35 nm. Figure 3 shows the mixture at 30% conversion. The figure shows crystalline silicon nitride particles, silica spheres and carbon black particles with a diameter of 35 nm. Figure 4 also shows the mixture at 30% conversion. Partially crystallised particles are shown, as well as an amorphous silica. The partially crystallised particles look rather inhomogeneous and a surface layer may be noticed as well. Figure 5 shows the mixture at 55% conversion. A  $\text{Si}_3\text{N}_4$  particle with no surface layer as well as carbon black particles is shown. Figure 6 also shows the mixture at 55% conversion. Amorphous silica, crystalline  $\text{Si}_3\text{N}_4$  particles and carbon black particles can be observed. Figure 7 shows the mixture at 97% conversion. Well crystallised  $\text{Si}_3\text{N}_4$  particles are

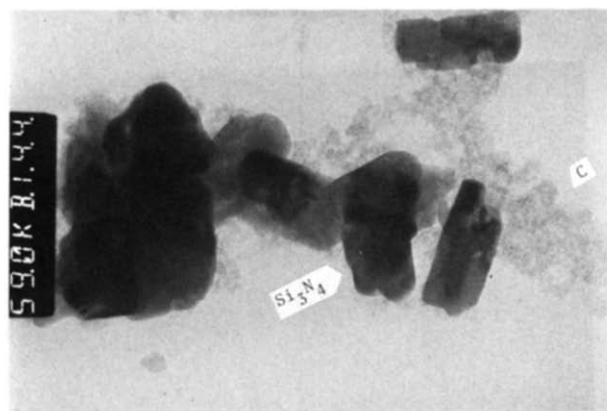
seen, mixed with carbon black. Figure 8 shows the mixture at 98.5% conversion. Well crystallised  $\text{Si}_3\text{N}_4$  particles with diameters less than 1000 nm are observed, mixed with carbon black particles with a diameter of 35 nm. Figure 9 shows a  $\text{Si}_3\text{N}_4$  particle at almost 100% conversion. This figure shows that the particle is well crystallised and is free of any surface layer.

Such a surface layer could have been an oxide or graphite. Figure 10 shows the mixture at almost 100% conversion. Well crystallised particles of  $\text{Si}_3\text{N}_4$  and carbon black particles with a diameter of 35 nm are shown.

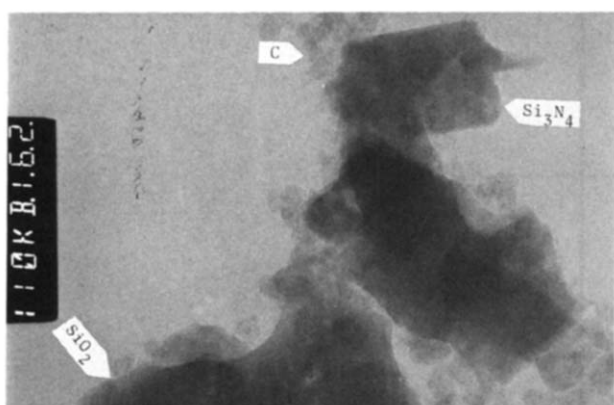
The results concerning the kinetics as measured in the thermobalance are given in Figs 11 to 14. These figures are obtained by converting the weight loss, from 1200°C onwards, to the conversion,  $a$ . Figure 11 shows the influence of the gas flow rate on the reaction rate of the synthesis of  $\text{Si}_3\text{N}_4$  at 1500°C measured for three tablets and for a  $\text{SiO}_2$ :C molar ratio of 1:2. Figure 12 shows the influence of the number of tablets and tablet size on the reaction rate



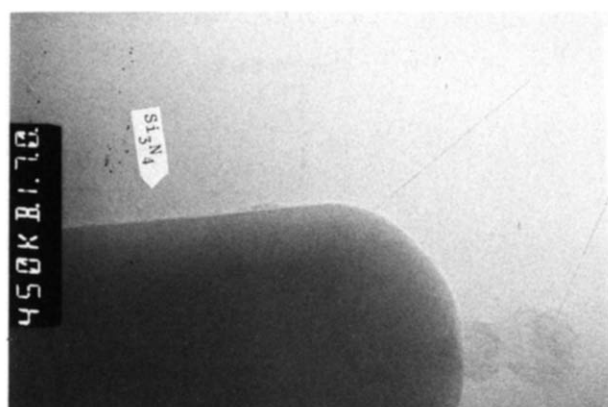
**Fig. 5.** The mixture at 55% conversion. The length of the black bar is 130 nm. Gas black particles with a diameter of 35 nm and a crystalline  $\text{Si}_3\text{N}_4$  particle are shown.



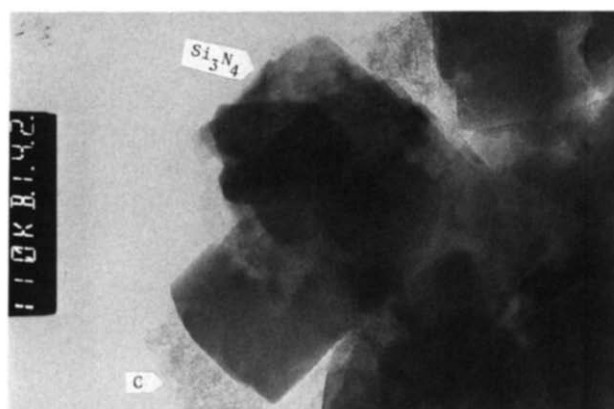
**Fig. 8.** The mixture at 98.5% conversion. The length of the black bar is 850 nm. The diameter of the  $\text{Si}_3\text{N}_4$  particles is less than 1000 nm and the diameter of the gas black particles is 35 nm.



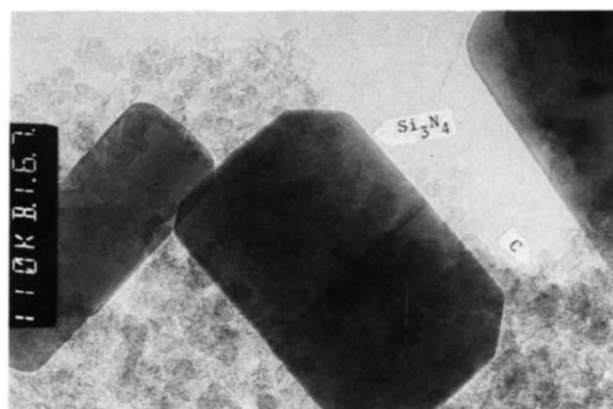
**Fig. 6.** The mixture at 55% conversion. The length of the black bar is 450 nm. The figure shows crystalline  $\text{Si}_3\text{N}_4$  particles, particles of gas black and amorphous silica.



**Fig. 9.** The mixture at 100% conversion. The length of the black bar is 110 nm. No surface layer on the  $\text{Si}_3\text{N}_4$  particle is observed.



**Fig. 7.** The mixture at 97% conversion. The length of the black bar is 450 nm. Well crystallised  $\text{Si}_3\text{N}_4$  particles as well as gas black particles are seen.



**Fig. 10.** The mixture at 100% conversion. The length of the black bar is 450 nm. The diameter of the gas black particles is 35 nm. The  $\text{Si}_3\text{N}_4$  particles are well crystallised.

of the synthesis of  $\text{Si}_3\text{N}_4$  at  $1500^\circ\text{C}$ , a gas flow rate of  $100\text{ cm}^3/\text{min}$  and a  $\text{SiO}_2:\text{C}$  molar ratio of 1:2. From these two figures it was assumed that measurement of the chemical reaction rate was best approached by taking one broken tablet for the synthesis and using a gas flow rate of at least  $100\text{ cm}^3/\text{min}$ . The particle size of the broken tablet is about 1 mm. Under these

reaction conditions physical aspects do not influence the reaction rate. Figure 13 shows the influence of the temperature on the reaction rate of the synthesis of  $\text{Si}_3\text{N}_4$  of one broken tablet, a gas flow rate of  $100\text{ cm}^3/\text{min}$  and a  $\text{SiO}_2:\text{C}$  molar ratio of 1:2. The results as presented in Fig. 13 were used to calculate the activation energy of the carbothermal synthesis

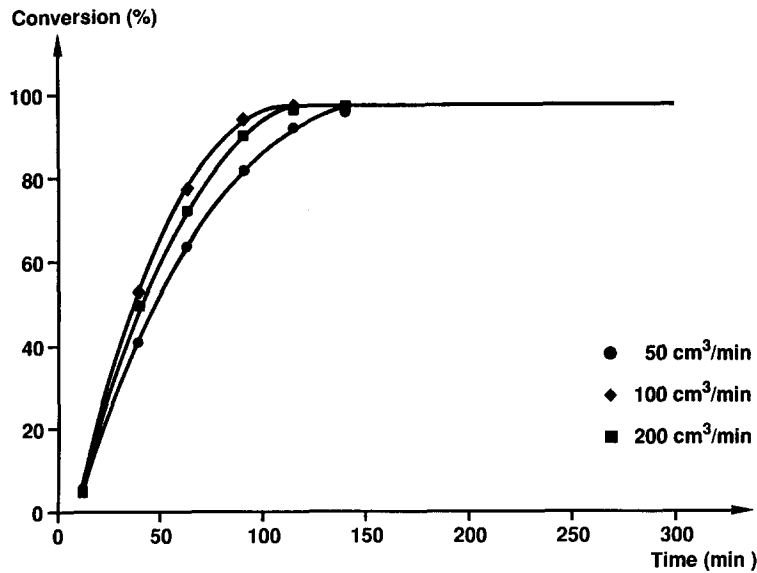


Fig. 11. The influence of the nitrogen flow rate on the reaction rate of three tablets in the thermobalance at 1500°C for C:SiO<sub>2</sub> = 2.

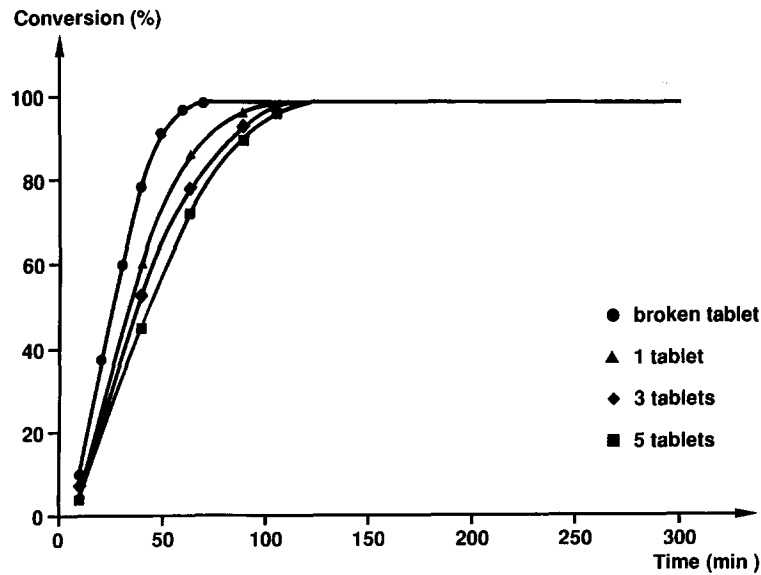


Fig. 12. The influence of the number of tablets and the tablet size on the reaction rate in the thermobalance. The nitrogen flow rate was 100 cm<sup>3</sup>/min, the temperature was 1500°C and the molar ratio C:SiO<sub>2</sub> = 2.

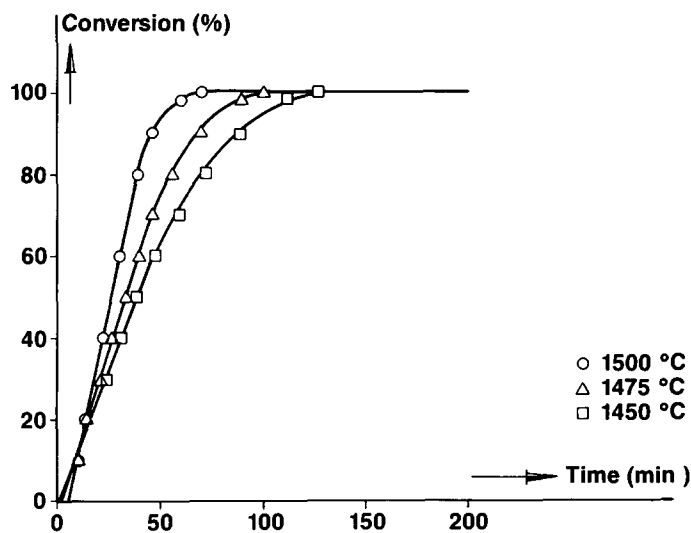


Fig. 13. The influence of the temperature on the reaction rate of one broken tablet in the thermobalance. The nitrogen flow rate was 100 cm<sup>3</sup>/min and the molar ratio C:SiO<sub>2</sub> = 2.

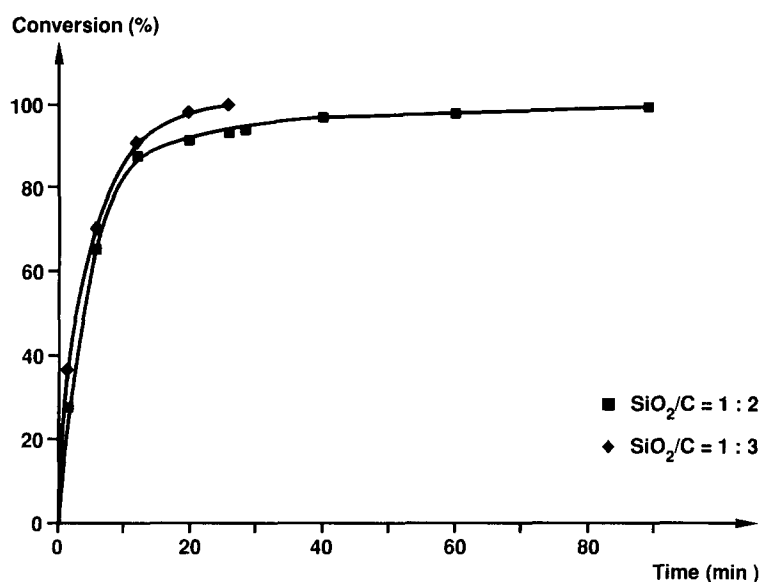


Fig. 14. The influence of the molar ratio  $\text{SiO}_2:\text{C}$  on the reaction rate in the thermobalance for one broken tablet at  $1490^\circ\text{C}$ . The nitrogen flow rate was  $100\text{ cm}^3/\text{min}$ .

of  $\text{Si}_3\text{N}_4$ . Figure 14 shows the influence of the  $\text{SiO}_2:\text{C}$  molar ratio on the reaction rate of the synthesis of  $\text{Si}_3\text{N}_4$  at  $1490^\circ\text{C}$  of one broken tablet and a nitrogen flow rate of  $100\text{ cm}^3/\text{min}$ .

The results of experiments concerning grain growth of  $\text{Si}_3\text{N}_4$  are given in Table 2. Results concerning grain growth as found in the literature are given as a log-log plot in Fig. 15.<sup>12</sup> These results show that grain growth of silicon nitride depends on

the chemistry of the silicon nitride powder and that grain growth is restricted to the smaller particles.

It was possible to produce a  $\text{Si}_3\text{N}_4$  powder with a specific surface area of  $15\text{ m}^2/\text{g}$ , a maximum grain size of  $0.5\text{ micron}$  and an alpha-phase content higher than 99%. The powder contains less than 200 ppm metallic impurities, less than 1.0 wt% carbon, less than 0.1 wt% free carbon and less than 1.7 wt% oxygen. The powder is free of whiskers. This result is

Table 2. Results of experiments concerning grain growth

Powder suppliers	Time (h)	Temperature ( $^\circ\text{C}$ )	O content (wt %)	Surface <sup>a</sup> O content (wt%)	Specific surface area ( $\text{m}^2/\text{g}$ )	Maximum grain size (micron)
Ube	—	—	1.5	1.1	11.6	1
Ube	1	1400	1.5	1.1		1
Ube	1	1500	1.3	0.9		1
Ube	1	1600	1.2	0.8		1
Ube	10	1400	1.2	0.8		0.5
Ube	10	1500	1.1	0.7		1
Ube	10	1600	1.1	0.7	10.1	0.5
Starck	—	—	2.1	1.1	19.7	1.5
Starck	1	1400	2.3	1.3		1.5
Starck	1	1500	2.0	1.0		1
Starck	1	1600	1.6	0.6		1
Starck	10	1400	1.9	0.9		1
Starck	10	1500	1.6	0.6		1.5
Starck	10	1600	1.3	0.3	9.1	1
Shin-Etsu	—	—	0.8	0.0	11.9	2
Shin-Etsu	1	1400	1.1	0.3		1.5
Shin-Etsu	1	1500	0.9	0.1		2
Shin-Etsu	1	1600	0.9	0.1		2
Shin-Etsu	10	1400	1.0	0.2		1.5
Shin-Etsu	10	1500	0.9	0.1		2
Shin-Etsu	10	1600	0.9	0.1	6.9	2

<sup>a</sup> Ube powder is estimated to contain 0.4 wt%, Starck powder 1.0 wt% and Shin-Etsu powder 0.8 wt% O in the crystal lattice.

Suppliers: Ube (Tokyo, Japan); Shin-Etsu (Tokyo, Japan); H. C. Starck (Berlin, Germany).

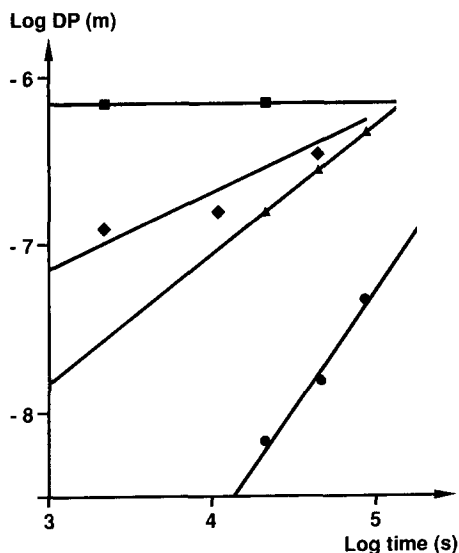


Fig. 15. Grain growth of  $\text{Si}_3\text{N}_4$  powder according to literature<sup>12</sup> as determined by measuring the specific surface area and converting this to the average particle size. ■ 1600°C, crystalline; ◆ 1500°C, crystalline; ▲ 1450°C, crystalline; ● 1400°C, amorphous.

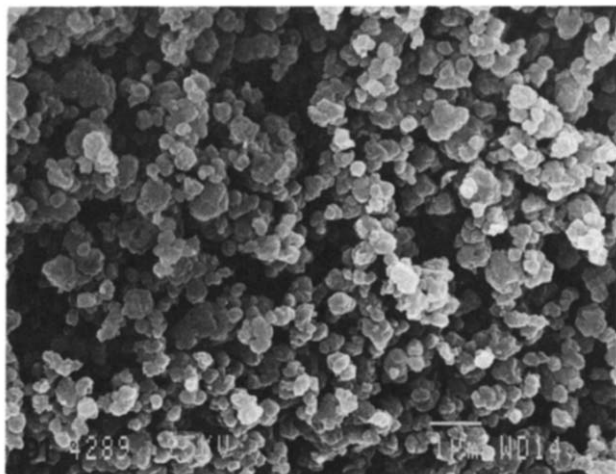


Fig. 16. Scanning electron micrograph of  $\text{Si}_3\text{N}_4$  powder after removal of free carbon. The length of the bar is 1000 nm. All particles are smaller than 1000 nm.

obtained by using pure, submicron raw materials, good mixing of the raw materials, the use of seeds, the use of dense granules, a proper choice of reaction conditions and removal of free carbon without oxidation of the product. An electron micrograph of the silicon nitride powder is shown in Fig. 16.

## 5 Discussion

The results from TEM concerning the reaction mechanism seem to indicate that the reaction mechanism is not simply  $\text{SiO}_2 + \text{C} = \text{SiO} + \text{CO}$  and  $3\text{SiO} + 3\text{C} + 2\text{N}_2 = \text{Si}_3\text{N}_4 + 3\text{CO}$ . The main argument for this is that after synthesis the carbon in the

product occurs as unreacted carbon black particles. The reaction mechanism mentioned suggests at least partial conversion of all carbon black particles and formation of  $\text{Si}_3\text{N}_4$  at the carbon black particles. As no  $\text{Si}_3\text{N}_4$  particles covered with thick layers of silica were observed, the reaction mechanisms of the carbothermal synthesis of  $\text{Si}_3\text{N}_4$  and SiC seem somewhat different. This explains the lower reaction rate for the synthesis of  $\text{Si}_3\text{N}_4$  as compared with the synthesis of SiC.<sup>13</sup> The synthesis of  $\text{Si}_3\text{N}_4$ , including prevention of whisker formation, was optimised by assuming solid-state diffusion as the reaction mechanism. This meant that a high density granulate and excellent mixing of silica, carbon and seeds were used. This approach was very successful. However, there is still room for discussion, considering diffusion paths or other reaction mechanisms.

From Fig. 13 the activation energy of the carbothermal synthesis of  $\text{Si}_3\text{N}_4$  was calculated. Two calculation methods were used. The first method was based on the curve at  $t = 0$ s. The curves were fitted with the formula  $da/dt = k$ . From this fit a value for the activation energy for the synthesis of  $\text{Si}_3\text{N}_4$  of 310 kJ/mol is found. The second method is based on curve fitting with Jander's equation:  $(1 - (1 - a)^{2/3})^2 = kt$ . This formula indicates that the reaction rate decreases as the conversion increases and this is in agreement with the observations. From this fit a value for the activation energy for the synthesis of  $\text{Si}_3\text{N}_4$  of 420 kJ/mol is calculated. Similar values for the activation energy for the carbothermal synthesis of SiC (440 kJ/mol according to Jander's equation<sup>13</sup>) and for the carbothermal synthesis of  $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$  (400 kJ/mol according to Jander's equation<sup>14</sup>) were found. It is believed that the activation energy of 420 kJ/mol is related to the coefficient of surface or volume diffusion of carbon in carbon black, as gas-phase or liquid-phase transport of carbon is excluded.

The observation that a higher C:SiO<sub>2</sub> molar ratio increases the reaction rate, especially at the end of the synthesis, may be explained in several ways. A higher C:SiO<sub>2</sub> ratio results in a higher metallic impurity content per mole of  $\text{Si}_3\text{N}_4$ , because the carbon black contains about 200 ppm of metallic impurities. Some of these impurities, such as Fe, Ca and Mg, act as 'catalysts'. A higher C:SiO<sub>2</sub> ratio results in a better degree of mixing of SiO<sub>2</sub>, C and seeds, especially at the end of the synthesis. When C:SiO<sub>2</sub> = 2, only a few carbon black agglomerates are available as a carbon source at the end of the reaction. These agglomerates are dispersed as a few isolated isles in an ocean of  $\text{Si}_3\text{N}_4$ . The same holds for the last silica particles. It is clear that the diffusion



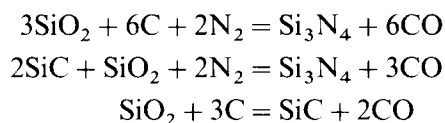
distances between silica and C are relatively long. When  $\text{C}:\text{SiO}_2 = 3$ , many carbon black agglomerates are available as carbon source and are well dispersed between  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  particles at the end of the reaction. It is clear that diffusion distances between silica and C are short.

The large atomic ratio of C/Si, as measured with ESCA, during and after synthesis, is most likely due to the difference in particle size between carbon black and silica or  $\text{Si}_3\text{N}_4$ . The SiC in the product is most likely present as a very fine material.

In accordance with the literature it was found that the larger  $\text{Si}_3\text{N}_4$  grains do not grow under the experimental conditions tested. This might be explained by assuming that small grains contain many defects in the crystal lattice, for instance caused by milling. By prolonged heating grain growth of small grains and defects healing occurs. When most defects have disappeared, grain growth stops. Therefore, it can be anticipated that the  $\text{Si}_3\text{N}_4$  powder, produced by carbothermal synthesis and the use of seeds, will always be a submicron powder. The high specific surface area of  $15 \text{ m}^2/\text{g}$  of the powder is mainly related to excellent mixing of the raw material and the use of seeds. The low content of SiC of the powder is related to the synthesis temperature of below  $1500^\circ\text{C}$  and the absence of metallic impurities such as Fe. From the literature it is known that  $\alpha$ - $\text{Si}_3\text{N}_4$  may contain up to about 1 wt% oxygen in the crystal lattice.<sup>15</sup> With TEM it was shown that the surface of the  $\text{Si}_3\text{N}_4$  particles contains very little silica or silicon oxynitride, if any. With ESCA it is shown that the  $\text{Si}_3\text{N}_4$  surface is enriched with oxygen. So a very thin layer ( $<0.5 \text{ nm}$ ) of oxygen or oxygen-containing compounds may be present. As there is oxygen present during the carbothermal synthesis of  $\text{Si}_3\text{N}_4$ , it cannot be prevented that oxygen is incorporated in the crystal lattice of the  $\text{Si}_3\text{N}_4$  grains. Therefore, it is believed that an oxygen content higher than 1.5 wt% is typical for carbothermally synthesised  $\text{Si}_3\text{N}_4$  powder.

It is assumed that the oxygen stabilises the alpha-modification, which explains the high alpha-content of the product. Aluminium stabilises the beta-modification through the formation of  $\beta$ '-SiAlON. When Al is absent, as in the present case, no  $\beta$ '-SiAlON can be formed.  $\beta$ - $\text{Si}_3\text{N}_4$  cannot be formed either, as no liquid phase is present, for example  $\text{FeSi}_x$ . It is assumed that the presence of SiO, certain metallic impurities and a porous  $\text{SiO}_2/\text{C}$  mixture leads to the formation of whiskers in the product. Whiskers are prevented by optimising the solid-state diffusion reaction mechanism and suppressing the

VLS or LS reaction mechanisms. The presence of some carbon in the product can be eliminated during the sintering process by holding the green ware at about  $1500^\circ\text{C}$  for some time. Then the following reactions will reduce both carbon and oxygen content of the green ware:



The metallic impurities originate from raw materials, additives and contamination.

For large-scale production a type of reactor with excellent heat transfer and gas–solid interaction is needed. This is due to the endothermic character of the carbothermal synthesis of  $\text{Si}_3\text{N}_4$ <sup>16</sup> and to the fact that this synthesis is also a gas ( $\text{N}_2$ , CO)–solid ( $\text{SiO}_2/\text{C}$ ) reaction. Such a type of reactor could be a fluidised bed. A fluidised bed reactor can be operated with an overall coefficient of heat transfer of about  $400 \text{ J}/(\text{m}^2 \text{ s})$ .<sup>17–19</sup>

The amount of nitrogen needed for the synthesis is important. Nitrogen is used for the synthesis of  $\text{Si}_3\text{N}_4$ , for the removal of CO and to keep the partial pressure of CO low in order to obtain a high reaction rate. The amount of nitrogen needed is important from the economic point of view and from the energetic point of view, as nitrogen is heated to reaction temperature.

## 6 Conclusion

Assuming that in the present case the reaction mechanism of the carbothermal synthesis of  $\text{Si}_3\text{N}_4$  is direct, solid-state diffusion appeared very successful. The value for the activation energy of the synthesis of  $\text{Si}_3\text{N}_4$  is  $420 \text{ kJ/mol}$ . This value is most likely related to the coefficient of diffusion of C atoms in carbon. Grain growth of  $\text{Si}_3\text{N}_4$  occurs, but is limited to smaller grains. Due to incorporation of oxygen in the crystal lattice, it is not possible to obtain a material with less than about 1.5 wt% oxygen. An excellent  $\alpha$ - $\text{Si}_3\text{N}_4$  powder can be obtained by the carbothermal synthesis.

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