

Synthesis of Silicon Nitride by Carbothermal Reduction and Nitriding of Silica: Control of Kinetics and Morphology

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Abstract

Reaction of finely dispersed high-purity silica and carbon in nitrogen flow begins at approximately 1250°C, and effective synthesis of α -silicon nitride was carried out at 1510–1550°C. Kinetics of the process is accelerated by seeding with a fine α -silicon nitride powder and the intensity of the seeding effect increases with increasing surface area of the seeding powder. The appropriate seeding and control of silicon monoxide evolution results in highly uniform and isometric α -silicon nitride crystals. If silicon monoxide evolved in the early stages of the reaction is not effectively consumed for silicon nitride growth, its reoxidation and redistribution of silica in the reaction mixture take place. Such heterogeneities, formed during the reaction, significantly slow down the overall process. These observations are consistent with a mechanism involving crystallisation of silicon nitride from gaseous silicon monoxide, carbon monoxide and nitrogen as the rate-limiting step. Silicon nitride is most probably formed in the sites where solid carbon is not present (i.e. in sites where carbon activity is lower than unity). The equilibrium temperature of the reaction $\text{Si}_3\text{N}_4 + 3\text{C} \rightleftharpoons 3\text{SiC} + 2\text{N}_2$ falls within the range 1510–1550°C (at 101 kPa N_2). An addition of free silicon to the reaction system promotes β -silicon carbide formation.

Die Reaktion fein verteilten Siliziumoxids und Kohlenstoffs unter fließendem Stickstoff beginnt etwa bei 1250°C. Die effektive Synthese von α -Siliziumnitrid wurde bei Temperaturen von 1510–1550°C durchgeführt. Die Kinetik des Prozesses wird durch den Impffzusatz feinen α -Siliziumnitrid-Pulvers beschleunigt, wobei die Intensität des Impfeffektes mit zunehmender Oberfläche des Impfpulvers steigt. Ein

geeignetes Impfen und die Kontrolle der Siliziummonoxid-Entwicklung führt zu sehr gleichförmigen und isometrischen α -Siliziumnitrid Kristallen. Wird das in den frühen Stadien der Reaktion gebildete Siliziummonoxid nicht ausreichend durch das Wachstum des Siliziumnitrids verbraucht, findet eine Rückoxidation und eine Rückverteilung des Siliziumoxids im Reaktionsgemisch statt. Solche während der Reaktion ausgebildeten Inhomogenitäten verlangsamen deutlich den gesamten Prozess. Diese Beobachtungen sind in Übereinstimmung mit einem Mechanismus, der als geschwindigkeitsbestimmenden Schritt die Kristallisation von Siliziumnitrid aus gasförmigem Siliziummonoxid, Kohlenmonoxid und Stickstoff enthält. Siliziumnitrid wird wahrscheinlich an Reaktionsorten gebildet, an denen fester Kohlenstoff nicht auftritt (also dort wo die Kohlenstoff-Aktivität geringer als 1 ist). Die Gleichgewichtstemperatur der Reaktion $\text{Si}_3\text{N}_4 + 3\text{C} \rightleftharpoons 3\text{SiC} + 2\text{N}_2$ fällt in das Temperaturintervall von 1510–1550°C (bei 101 kPa N_2). Die Zugabe von freiem Silizium zum Reaktionssystem beschleunigt die Bildung von β -Siliziumcarbid.

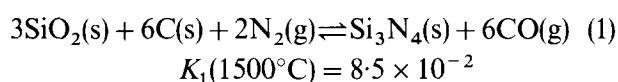
De la silice et du carbone très purs et finement dispersés placés dans un flux d'azote commencent à réagir approximativement à 1250°C et la synthèse effective de la phase α - Si_3N_4 a lieu entre 1510–1550°C. La cinétique de la réaction peut être accélérée par ensemencement par une poudre fine de α - Si_3N_4 , et ce d'autant plus que la poudre utilisée possède une surface spécifique importante. Un ensemencement approprié et le contrôle de la formation de SiO conduisent à des cristaux de α - Si_3N_4 très uniformes et cubiques. Si le SiO formé dans les premières phases de la réaction n'est pas effectivement consommé pour la croissance de Si_3N_4 , il est réoxydé et la redistribution

de silice dans le mélange réactionnel a lieu. De telles hétérogénéités formées pendant la réaction ralentissent considérablement l'ensemble du processus. Ces observations sont compatibles avec un mécanisme impliquant la cristallisation de Si_3N_4 à partir de SiO gazeux, CO et azote, laquelle jouerait le rôle de l'étape limitante. Si_3N_4 est très certainement formé dans les sites exempts de carbone sous forme solide (c'est à dire dans des sites où l'activité du carbone est inférieure à 1). La température d'équilibre de la réaction $\text{Si}_3\text{N}_4 + 3\text{C} \rightleftharpoons 3\text{SiC} + 2\text{N}_2$ tombe dans l'intervalle 1510–1550°C (à 101 kPa N_2). L'addition de silicium libre au système réactionnel favorise la formation de β -SiC.

1 Introduction

Carbothermal reduction and nitriding of silica has been recognised as an effective method for the synthesis of reasonable quality and sinterable α -silicon nitride powders.^{1–16} What do we know about the process?

Formation of silicon nitride from silica and carbon in nitrogen flow is described by the following overall reaction:



where K_1 is the equilibrium constant of reaction (1) at 101 kPa calculated from the data in Ref. 17. Despite the low value of the equilibrium constant practically full conversion to silicon nitride can be achieved at 1400–1500°C when carbon monoxide is removed from the system.

Various sorts of silica of different purity and specific surface areas have been used as starting materials—synthetic amorphous xerogels and monosized powders^{1–5,7–10,12,15} and natural raw materials, e.g. milled cristobalite rocks^{6,14} and layered polysilicate magadiite.¹¹ Silica powders are mixed with carbon blacks in different ratios, typically 1:3–1:15 (by moles). Homogeneous mixture of silica and carbon was obtained by pyrolysis of rice husks in Ref. 16. Reaction mixtures were heated in nitrogen flow at temperatures of 1350–1500°C for several hours. In recent work¹⁸ a temperature as high as 1550°C could be used for silicon nitride formation from very pure silica-carbon mixtures prepared by a sol-gel mixing route. Poor data on the arrangement of the experiments are available but, concerning the resulting products, basic information is as follows.

- High-purity reaction systems produce relatively pure silicon nitride powders with high α -

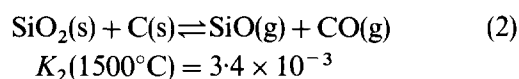
phase content, pillar-like morphology, narrow size distribution and with particles sizes about 1–5 μm .

- Transition metal impurities, e.g. iron, nickel and vanadium compounds (in mass% of the order of 10^{-1} – 10^0), increase the rate of silicon nitride formation but also increase the β -silicon nitride and β -silicon carbide contents, especially at temperatures above 1450°C.
- Some results⁷ indicate that higher specific surface areas of the starting reactants are advantageous. However, this effect is not unambiguous.
- The effect of nitrogen flow rate cannot be evaluated exactly. Hundreds–thousands cm^3/min of N_2 were used in Ref. 10, and it was shown that 30–80 cm^3/min of N_2 per 1 g of silica in the starting mixture is sufficient to keep carbon monoxide concentration in the outlet gas below 15 vol.%.
- The presence of 5 vol.% of hydrogen in the nitriding gas was found to accelerate the silicon nitride formation from rice husks in Ref. 16.
- It has been proved that seeding has the most remarkable effect on silicon nitride formation. When 5–10 mass% of fine α -silicon nitride crystals are added to the starting silica-carbon mixture, the formation of α -silicon nitride is accelerated, the size of crystals produced is reduced and their morphology becomes more uniform.
- Weakly agglomerated silicon nitride powders with specific surface area up to 10 m^2/g , α -phase content more than 95%, oxygen content 2–3 mass% and carbon content below 1 mass% are produced when sufficiently pure reactants and optimum reaction conditions are used.
- Some part of the α -silicon nitride crystals in the form of whiskers is usually found in the reaction products. The whiskers grow mostly in areas out of the reaction mixture.

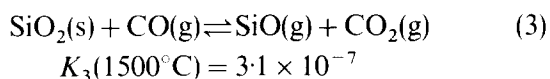
2 Thermodynamics

Formation of silicon nitride by carbothermal reduction and nitriding of silica is generally considered to consist of two principal reaction steps.

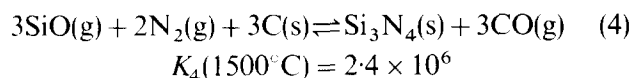
The first step is agreed to be the reduction of silicon dioxide to silicon monoxide by the following reactions:



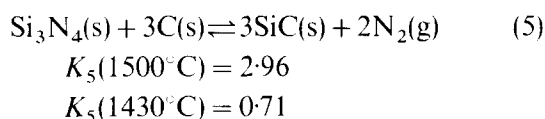
or



Two reaction schemes were proposed for the second reaction step. Komeya and Inoue¹ suggested that gaseous silicon monoxide reacts with nitrogen on the surface of carbon particles:

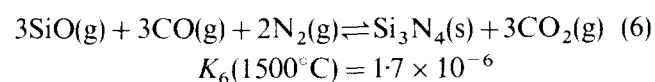


This reaction can occur rapidly until the whole surface of the carbon particles is covered by a silicon nitride layer. Further reaction could proceed by diffusion of reactants through this layer. In such a case a morphology of silicon nitride similar to that of the carbon particles would be expected. Such behaviour has not been found experimentally; however, some other authors^{8,13,15} have considered this reaction to proceed in the formation of silicon nitride. Moreover, formation of silicon nitride in contact with solid carbon is thermodynamically possible only up to about 1440°C. At higher temperatures silicon nitride is not stable in the $\text{SiO}_2(\text{s})\text{--C}(\text{s})\text{--N}_2(\text{g})\text{--Si}_3\text{N}_4(\text{s})$ system (at 101 kPa) and silicon carbide should be preferably formed if overpressure of nitrogen is not used:

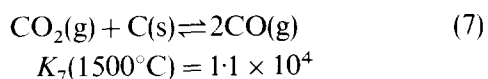


Since silicon nitride is commonly produced at 1500°C in the pure reaction system, activity of carbon lower than unity is to be considered in the sites where silicon nitride crystals are formed. If the carbon activity is considered to be of unity, silicon carbide could be formed also below 1440°C. It would be the case when the partial pressure of nitrogen drops below about 0.84 at 1430°C, as follows from the K_5 value. That is why the concentration of carbon monoxide is to be kept below about 16 vol.% (at 1430°C and 101 kPa). It is obvious that the above considerations are based on the thermodynamic data used.¹⁷

According to Zhang and Cannon⁷ the morphology of silicon nitride crystals strongly indicates their formation by a gas-phase reaction:



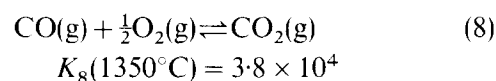
followed by



From the uniform particle size of the silicon nitride

they proposed that supersaturation of silicon monoxide necessary for the nucleation of silicon nitride can be achieved only during the initial stages of the reaction, resulting in one generation of crystals. From this viewpoint the importance of seeding of the initial silica-carbon mixture with a fine silicon nitride powder for increasing the rate of silicon nitride formation and for decreasing the particle size of the product seems to be obvious.

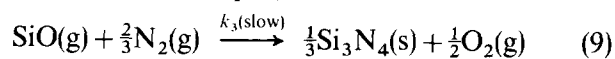
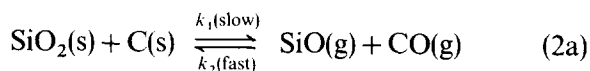
Since carbon dioxide is readily reduced in the presence of excess carbon it is hardly difficult to measure experimentally its actual partial pressure in the reaction mixture by conventional IR or mass spectroscopy or thermal conductivity methods. The problem was successfully solved by Wada and Wang,¹⁹ who used a Mo/Mo-MoO₂/stabilised cubic ZrO₂ solid electrolyte cell to monitor the actual oxygen partial pressure in the silica-carbon mixture during silicon carbide and silicon nitride formation (small amounts of NaF or Na₃AlF₆ were added to the starting mixtures to promote the whisker-like crystal formation). During heating a rapid increase of oxygen partial pressure from about 10⁻¹³ Pa at 1260°C to about 10⁻⁶ Pa at 1350°C was found. After reaching the temperature of isothermal holding (1350°C) the oxygen partial pressure was maintained at the maximum value for about 3 h and then continuously decreased as the reaction proceeded. From the given maximum oxygen partial pressure the maximum ratio P_{CO_2} to P_{CO} of about 0.1 can be estimated according to the equilibrium:



As was shown in Ref. 10, the maximum concentrations of carbon monoxide in the outlet gas on carbothermal reduction of silica can achieve 10–20 vol.% (depending on the temperature and nitrogen flow rate), from which the local concentrations of carbon dioxide in the reaction mixture of the order of per hundreds or of per thousands can be estimated at the early stages of the reaction. Therefore it seems to be reasonable to include the reactions producing oxygen (or carbon dioxide), e.g. reactions (3) and (6), in the mechanism of silicon nitride formation, despite the presence of the fluorides used in Ref. 19, which might somewhat change the reaction conditions compared with that in the pure silica-carbon mixture. Moreover, high concentrations of oxygen (or carbon dioxide), as estimated above, can play a significant (negative) role in silicon nitride formation by carbothermal reduction and nitriding of silica.

A reasonable reaction sequence during the silicon

nitride formation process, including qualitative estimation of reaction rate constants, has been proposed by Rahman and Riley:¹⁶



It is obvious that the rate constants strongly depend on the actual conditions in the reaction mixture and they are changed in time. However, it can be accepted that silicon monoxide evolved during silica reduction must be immediately consumed for silicon nitride growth. If not, it is readily reoxidised to silicon dioxide, not only by reaction (2a) from right to left but also by oxygen (or carbon dioxide) arising in the system. The authors¹⁶ proposed the equation for the overall silicon nitride formation rate, $f(\text{Si}_3\text{N}_4)$:

$$f(\text{Si}_3\text{N}_4) = aSk_3P_{\text{SiO}}P_{\text{N}_2} \quad (11)$$

where a is a constant and the term S is proportional to the concentration of reaction sites. Equation (11) corresponds well to the numerous previous works in which an acceleration of silicon nitride formation due to seeding and nitrogen flow rate increase was observed.

In the present work kinetic and morphological aspects of carbothermal reduction and nitriding of silica were studied in more detail.

3 Experimental

3.1 Preparation of reaction mixtures

Two different silicas and carbon blacks were used as starting materials:

- (1) Aerosil OX-50 (Degussa, Germany)—high-purity finely dispersed amorphous silica, $S_{\text{BET}} = 50 \text{ m}^2/\text{g}$;

- (2) quartz powder—fraction below $5 \mu\text{m}$, $S_{\text{BET}} = 5 \text{ m}^2/\text{g}$;
- (3) acetylene carbon black—high-purity, ash content 0.1 mass%, metallic impurities about 0.01%, $S_{\text{BET}} = 80 \text{ m}^2/\text{g}$;
- (4) pigment grade carbon black—ash content 1.0 mass% (V, Ni ≈ 0.1 – 0.5% ; Fe, Al $\approx 0.01\%$; Ca, Mg $< 0.01\%$), $S_{\text{BET}} = 1000 \text{ m}^2/\text{g}$.

Silica-carbon mixtures of 1:1 mass ratio (1.5 by moles) were prepared by dry milling in an agate planetary mill for 30 min. Various fine silicon nitride powders of 0, 5, 10 and 20 mass% were added to the starting mixtures as seeding materials. Fine silicon particles ($d \approx 0.2 \mu\text{m}$) prepared by pyrolysis of silane at 800°C under argon were also used as the addition in one experiment. Homogeneity of the starting mixtures was controlled by optical microscopy. No large inhomogeneities were observed in the mixtures.

The mass of the batch in a reactor was changed to keep a constant content of silica of 6 g with acetylene carbon black mixtures and 3 g with pigment carbon black mixtures, respectively. Nitrogen flow (at 25°C) was 15 – $30 \text{ dm}^3/\text{h}$.

Data on the seeding powders and on the experiments are summarised in Tables 1–3.

3.2 Reactor

Reaction mixtures were heated in a packed-bed graphite reactor at $1510 \pm 10^\circ\text{C}$ for 1.5–9 h. Additional experiments at 1550 and 1590°C were also carried out.

The reactor similar to that described in Refs 10 and 20 was designed to give a sufficient supply of nitrogen to the reaction mixture and an efficient removal of carbon monoxide out of the reaction mixture (Fig. 1). Nitrogen entered the reactor through the inlet perforated tube (1), passed through the reaction mixture (5) and exited through the

Table 1. Data on silicon nitride powders used for seeding in carbothermal reduction and nitriding of silica

Number	Seeds	Chemical composition (mass%)			Content of α - Si_3N_4 (mass%)	S_{BET} (m^2/g)
		N	O	C		
I ^a	SCR-1	36.4	2.2	1.4	100	<2
II ^a	SCR-2	37.1	1.7	0.5	98	8.0
III ^b	LC-12	38.6	1.8	0.2	95	20.9
IV ^c	PCS	34.1	5.9	0.2	30- α 20- β 50-amorphous	22.3

^aI, II—prepared by silicon carbothermal reduction.

^bIII—prepared by silicon nitriding.

^cIV—prepared by plasma-enhanced CVD.

Table 2. Data on the experiments in carbothermal reduction and nitriding of silica (silica and carbon mixtures with 1:1 mass ratio, nitrogen flow rate 250 cm³/min at 25°C)

Experiment number	Starting material		10 mass% of SCR-2 seeds	Mass of starting mixture (g)	Time at 1510°C (h)
	Silica	Carbon			
1	Aerosil	Acetylene black	No	12	8
2	Quartz	Acetylene black	No	12	8.3
3	Aerosil	Pigment black	No	6	3.5
4	Aerosil	Acetylene black	Yes	13.2	4.2
5	Quartz	Acetylene black	Yes	13.2	4.5
6	Aerosil	Pigment black	Yes	6.6	2.5
7	Aerosil	Acetylene black	No	12	1.5
8	Aerosil	Acetylene black	No ^a	13.2	6.0

^a Added 10 mass% of fine silicon ($d \approx 0.2 \mu\text{m}$) prepared by silane pyrolysis.

Table 3. Experimental conditions in carbothermal reduction and nitriding of silica (12 g of 1:1 by mass Aerosil and acetylene carbon black mixture, 250 cm³/min of N₂ at 25°C)

Experiment number	Seeds	Mass% of seeds	Time at 1510°C (h)
1 ^a	None	0	8.0
4 ^a	SCR-2	10	4.2
9	SCR-1	10	5.8
10	SCR-2	5	6.6
11	SCR-2	20	3.0
12	LC-12	10	4.5
13	PCS	10	3.5

^a Numbers 1 and 4 are the same experiments as in Table 2.

crucible wall that served as a filter. Nitrogen was dried and deoxidised by passing through a chromium(II) oxide-silica gel absorption column. Temperature was measured by PtRh6/PtRh30 thermocouple (2) protected by an alumina tube (3). The temperature gradient along the reactor height was about 20°C. The reactor was placed vertically in

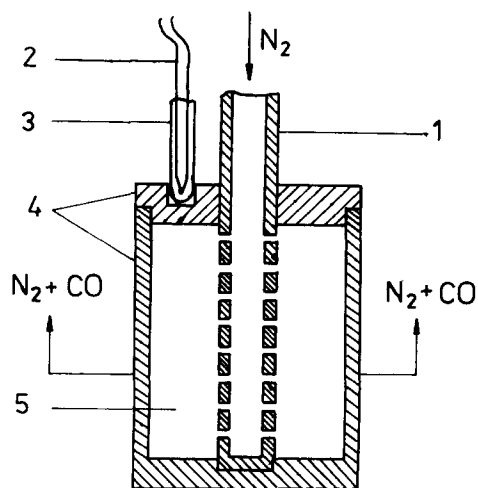


Fig. 1. Graphite reactor: (1) inlet perforated tube, (2) thermocouple, (3) protecting alumina tube, (4) crucible with lid and (5) reaction mixture.

a protecting alumina tube and heated in an adapted laboratory chamber furnace. The heating rate was 10°C/min up to 1300°C; above 1300°C it was 5°C/min.

3.3 Analytical methods

The rate of the reaction (and conversion extent) was continuously recorded by measuring the carbon monoxide concentration in the outlet gases with a carbon monoxide analyser (Infralyt 4, VEB, Junkalor Dessau, Germany). After the reaction non-reacted excess carbon was eliminated by oxidation treatment at 700°C for several hours.

The morphology of the starting materials and the products was inspected by optical and electron microscopy. The products were analysed by X-ray powder diffraction analysis for phase composition, by activation neutron analysis for oxygen content, and by LECO for carbon content. Nitrogen content was determined from the amount of ammonia evolved during fusion, the samples at 700°C with an excess of CaO-NaOH (1:1 mass ratio) powdered mixture.

4 Results and Discussion

4.1 Effect of starting materials

Data on the experiments are summarised in Table 2. Chemical and phase compositions, and specific surface areas of the products, are given in Table 4. Given phase compositions were calculated from chemical analyses and they corresponded well with the X-ray powder diffraction phase analyses.

The rates of silica reduction are represented in Fig. 2 by the dependences of actual carbon monoxide concentrations in the outlet gas (in vol.%) versus time, where negative times correspond to the heating-up periods, and $\tau = 0$ is the time at which the

Table 4 Chemical and phase compositions and specific surface areas of the products

Number	Content (mass%)			Phase composition ^a (mass%)			S_{BET} (m^2/g)	
	N	C	O	Si_3N_4		SiO_2		
				Total	β			
1	27.0	1.2	14.0	68	tr ^b	4	28	3.5
2	37.2	1.1	2.2	93	tr	3	4	2.5
3	24.5	10.2	3.3	60	30	34	6	—
4	37.9	0.7	2.2	94	tr	2	4	4.8
5	37.5	0.6	2.5	93	tr	2	5	—
6	31.7	4.4	3.5	79	15	14	7	—
7	9.6	—	—	23	—	—	77	—
8	31.4	5.0	4.2	75	tr	17	8	—
9	36.3	1.2	2.9	91	0	4	5	3.0
10	35.6	1.1	3.0	89	tr	4	7	4.7
11	38.1	0.4	2.2	95	tr	1	4	4.8
12	36.4	0.5	3.6	91	tr	2	7	9.2
13	33.0	2.7	3.8	83	10	9	8	6.9

^a Calculated from chemical analyses.

^b tr—traces.

temperature of isothermal holding is achieved. Reduction of silica with high-purity carbon black begins at about 1250°C, and that with the low-purity carbon about 100°C earlier. Maximum carbon monoxide concentrations are observed in the first minutes of isothermal holding. Reduction of silica with low-purity carbon is much faster, more

probably due to the impurities (especially the transition metals) present in the carbon than due to a higher specific surface area. However, it is to be noted that the product consists of only 60 mass% of silicon nitride and of more than 30% of β -silicon carbide (Table 4, product number 3). Moreover, silicon nitride consists of about 70% of α -phase and of about 30% of β -phase. The products prepared from the mixtures with high-purity carbon (numbers 1 and 2) consist practically only of α -silicon nitride and silicon carbide was not detected in significant amounts.

There is a remarkable difference between the kinetics of reduction of Aerosil and quartz powders (Fig. 2). After rapid reaction in early stages the rate of reduction of Aerosil is remarkably slowed down and the reaction proceeds at a constant rate for several hours. About 70% conversion to silicon nitride was achieved after 8 h of isothermal holding. Reaction of coarser quartz powder is about 1.5 times slower in the initial stages but it is substantially more continuous and practically full conversion to silicon nitride is achieved after 8 h. When 10 mass% of fine α -silicon nitride powder was added to the starting mixtures the difference between the Aerosil and quartz behaviour practically disappeared (Fig. 3), and the reactions were completed in about half the time of the case without seeding.

A reason why the rate of reaction of Aerosil with high-purity carbon (without seeding) drops in such a significant way can be as follows. At the beginning the reaction mixture is highly dispersed and homogeneous; this leads to rapid silica reduction

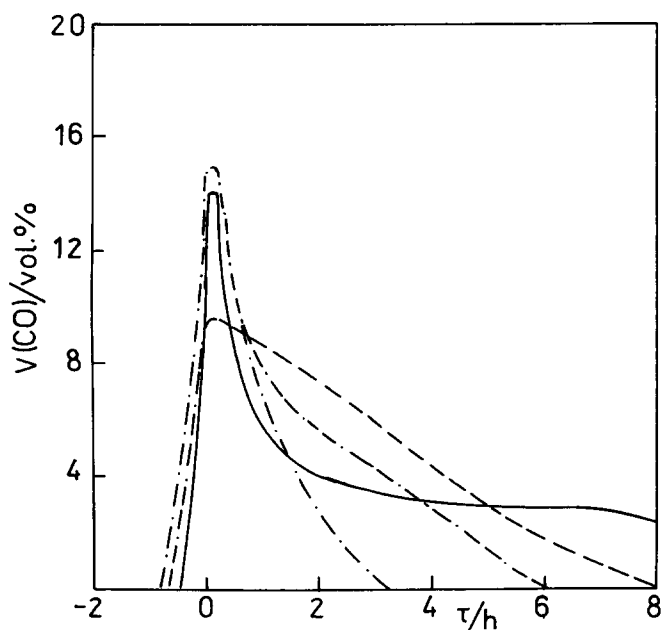


Fig. 2. Actual concentrations of CO in outlet gases at carbothermal reduction and nitriding of silica (without seeding, 1510°C, 250 cm^3/min of N_2): (—) no. 1, Aerosil + acetylene black; (---) no. 2, quartz + acetylene black; (-·-·-) no. 3, Aerosil + pigment black (mass of the reaction mixture 6 g); and (----) no. 8, Aerosil + acetylene black, 10 mass% of fine silicon added.

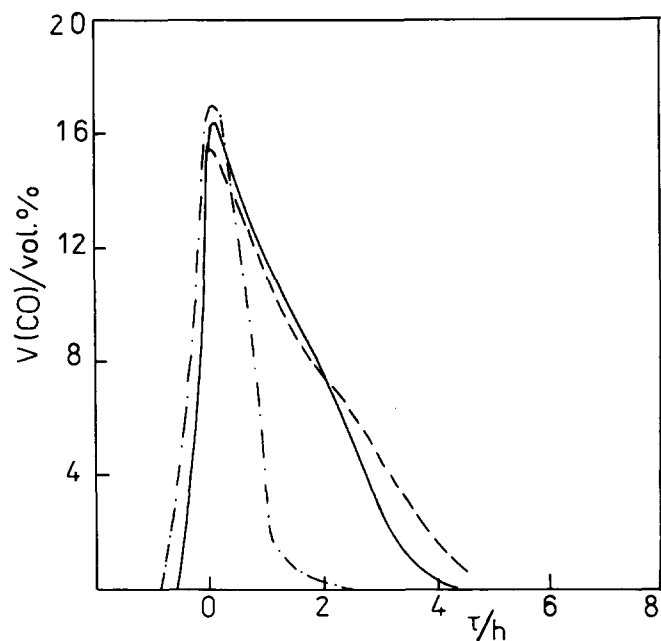


Fig. 3. Actual concentrations of CO in outlet gases at carbothermal reduction and nitriding of silica (10 mass% of SCR-2 seeds added, 1510°C, 250 cm³/min of N₂): (—) no. 4, Aerosil + acetylene black; (---) no. 5, quartz + acetylene black; and (-·-·-) no. 6, Aerosil + pigment black (6.6 g of the reaction mixture).

and great evolution of silicon monoxide. The amount of silicon monoxide evolved probably exceeds the amount that can be consumed for silicon nitride formation because of a lack of sufficient silicon nitride surface in the early stages of the reaction. This means that spontaneous nucleation of silicon nitride is rate limiting in the first reaction stages. The excessive silicon monoxide can escape from the reactor or can be reoxidised to silicon dioxide. The latter case can cause a redistribution of silica in the reaction mixture. Experiment number 7 is related to the above considerations. The reaction was interrupted after 1.5 h of isothermal holding at about 25% conversion level. The resulting mixture (still with carbon) is shown in Figs 4(a) and (b). Large (20–50 μm) white, most probably silica, inhomogeneities are observed in the mixture. During subsequent heating the silica aggregates can sinter and crystallise to form large, dense silica grains that can hardly be reduced. Typical cristobalite crystals formed during 8 h isothermal heating are shown in micrographs in Figs 4(c) and (d) (sample after carbon burning out). From these figures it also follows that the surfaces of cristobalite grains serve for heterogeneous nucleation and growth of hexagonal α-silicon nitride crystals, as indicated by the phase composition of the sample: 70 mass% α-silicon nitride, 26% silica (α-cristobalite and amorphous) and 3% β-silicon carbide. This observation supports

the consideration presented in Section 2 above that silicon nitride is preferably formed in sites with low activity of carbon.

In the case with quartz powder the redistribution of silica is less probable, because of the slower initial reduction rate, and that is why the conversion to silicon nitride is more equitable.

Catalytic activity of the impurities present in the pigment carbon is not clear and it can have several reasons. First, the transition metals are well known to readily change their oxidation states, so they can remarkably accelerate transport of oxygen in the system. Second, formation of some amount of a liquid phase cannot be excluded, as indicated by increased amounts of β-silicon nitride in product numbers 3 and 6 (Table 4). Both these effects could accelerate the silica reduction, the latter by improving the contact between silica and carbon grains. In this way large amounts of silicon carbide found in the products could also be explained. Moreover, the transition metals are known to shift the Boudouard equilibrium ($2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$) by supporting the disintegration of carbon monoxide and formation of carbon and carbon dioxide.²¹ Consequently activity of carbon can be increased to some extent in sites in the reaction mixture, where solid carbon is not present. Another effect of the metallic impurities may be increasing the activity of silicon in the system. Although no free silicon was detected in any product, its formation, as an intermediate, could proceed by decomposition of silicon monoxide ($2\text{SiO} \rightleftharpoons \text{Si} + \text{SiO}_2$) and by its dissolution in a silicide melt, formation of which could be possible. Since carburisation of silicon is known to be fast, especially above its melting point, simultaneous formation of silicon carbide is to be expected. Experiment number 8 is related to this consideration. The addition of 10 mass% of fine silicon powder to the Aerosil–acetylene carbon black mixture led to an acceleration of the silica reduction (Fig. 2), and a remarkably larger amount of β-silicon carbide was found in the product (Table 4). This result does not necessarily mean that silicon is formed as an intermediate during carbothermal reduction of silica with the low-purity carbon. However, it indicates that when silicon appears in the reaction system it more likely reacts with carbon to form silicon carbide than with nitrogen to form silicon nitride (at given experimental conditions). The morphology of the product is shown in Fig. 9(b). There is no doubt that the large, perfectly shaped grains are hexagonal crystals of α-silicon nitride. The small particles are most probably β-silicon carbide crystals which morphology corresponds to the

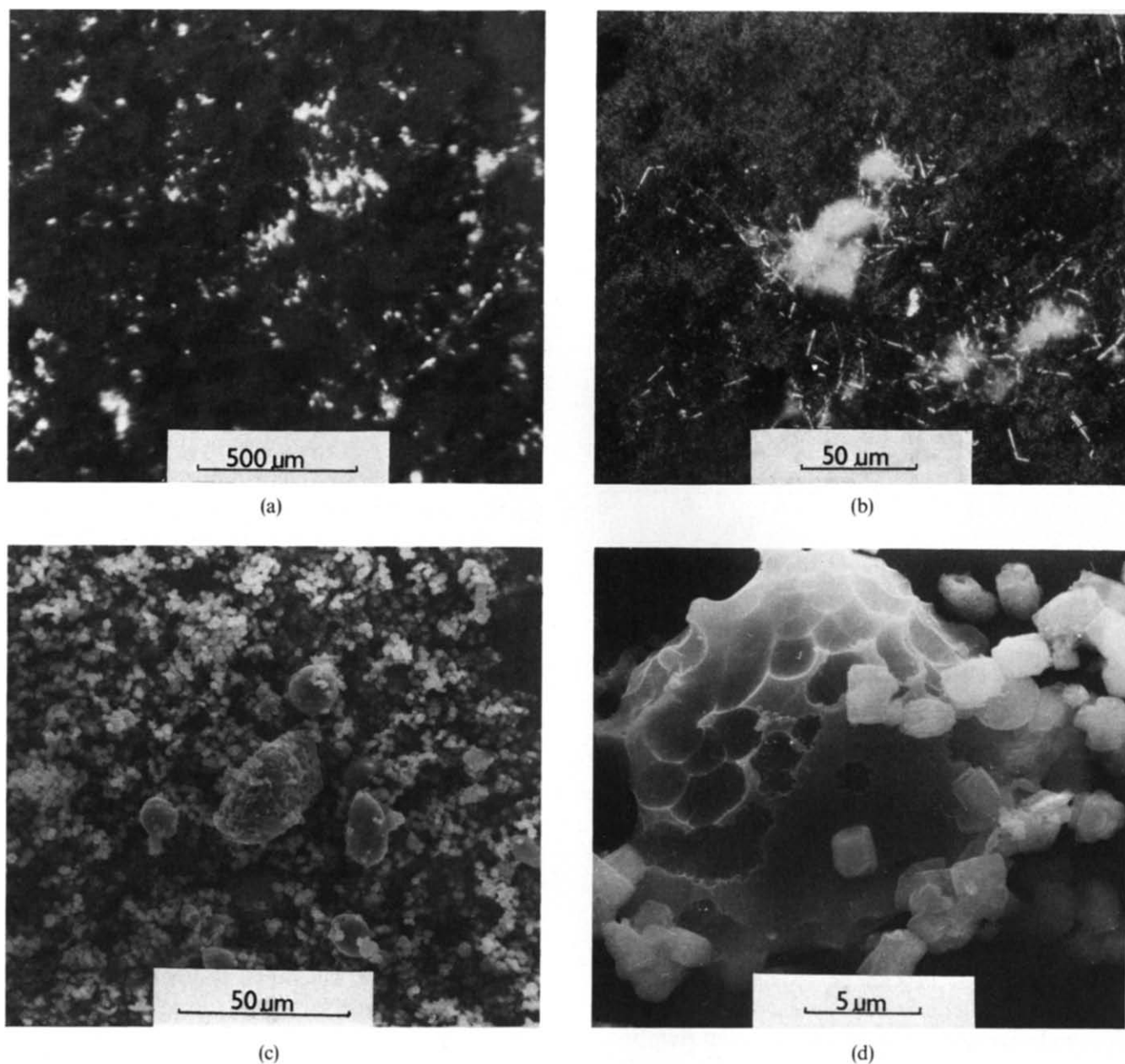


Fig. 4. Micrographs: (a),(b) silica agglomerates formed during heating the Aerosil + acetylene black mixture (experiment number 7); (c),(d) large cristobalite grains formed during prolonged heating period; hexagonal α -silicon nitride crystals are formed on their surfaces (phase composition of the sample: 70% α -silicon nitride, 26% silica—cristobalite and amorphous, 4% β -silicon carbide).

morphology of the added silicon powder (see phase composition given in Table 4).

4.2 Effect of seeding

In further experiments the effect of seeding of starting silica-carbon mixtures with fine silicon nitride powders of various quality and amounts on the kinetics of the process was investigated in more detail. Data on seeding powders and on the experiments are given in Tables 1 and 3. Experiment numbers 1 and 4 in Table 2 are also included in this series of the work.

The effects of various silicon nitride types as

seeding additives are compared in Fig. 5. There is a remarkable difference between the effects of coarse SCR-1 (number I) and the other seeding materials. On the other hand, slight differences in the reaction rates with the finer numbers II-IV seeding powders indicate that the surface of the seeding silicon nitride powder of about $1.5\text{--}3.5\text{ m}^2$ per 1 g of silica in the starting mixture is sufficient to effectively consume the silicon monoxide evolved, thus promoting the silica to silicon nitride conversion rate.

The positive influence of the increasing amount or of the total surface of seeding silicon nitride crystals on the reaction rate is clearly shown in Fig. 6, where

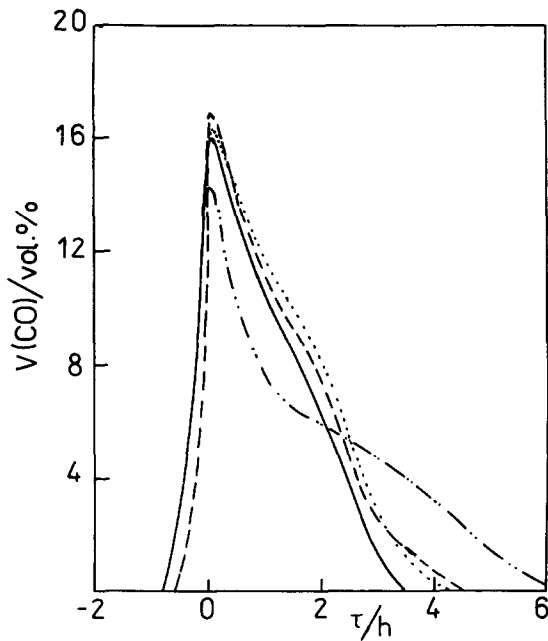


Fig. 5. The effect of various seeding additives on the kinetics of carbothermal reduction and nitriding of silica (10 mass% of seeding added to Aerosil+acetylene black mixture, 1510°C, 250 cm³/min of N₂): (—) PCS, (---) LC-12, (· · ·) SCR-2 and (- · - ·) SCR-1.

various amounts of fine α -silicon nitride powder prepared by silica carbothermal reduction (SCR-2) were used. The evolution of silica reduction (or the degree of its conversion to the intermediates and the products) is expressed in Figs 7 and 8 by the portions of carbon monoxide produced during the process, where 100% carbon monoxide corresponds to the

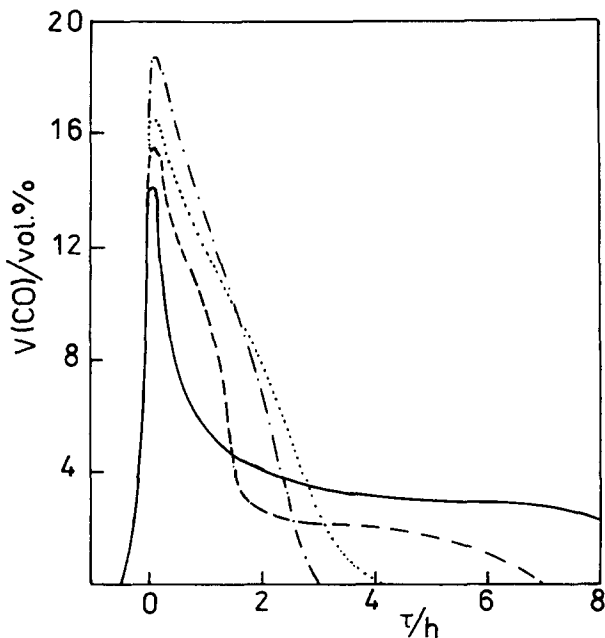


Fig. 6. The effect of the amount of SCR-2 seeds on the kinetics of carbothermal reduction and nitriding of silica (Aerosil+acetylene black mixture, 1510°C, 250 cm³/min of N₂). Mass % of seeds: (—) 0, (---) 5, (· · ·) 10 and (- · - ·) 20.

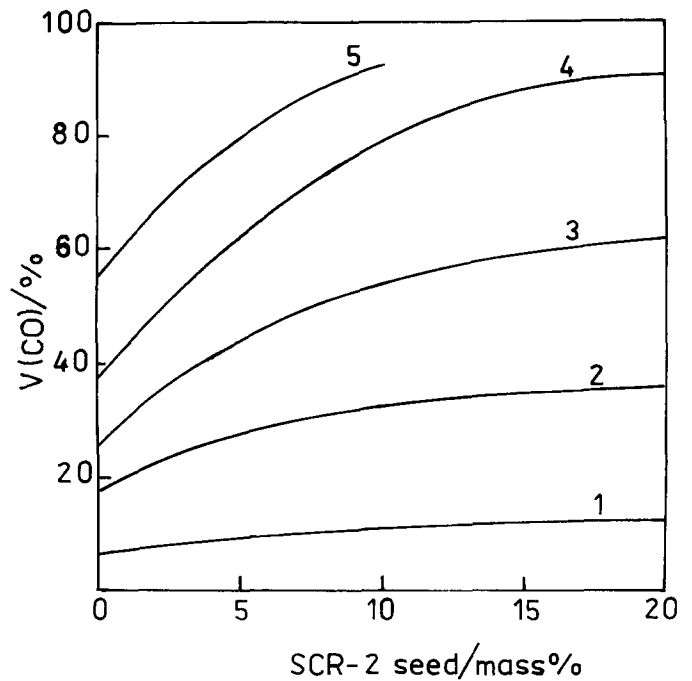


Fig. 7. Evolution of silica reduction expressed in vol.% of total amount of CO evolved; 100% CO corresponds to the completeness of silica reduction (Aerosil+acetylene black mixture seeded with 0, 5, 10 and 20 mass% of SCR-2, 1510°C, 250 cm³/min of N₂). Actual time of the reaction (h): (1) 0, (2) 0.5, (3) 1.0, (4) 2.0 and (5) 4.0.

completion of reaction (1). The greatest conversion increments (at a given time) are observed between 0% and 5% seeding levels, and they are subsequently decreased as the amount of the seeds is increased.

The effect of seeding by the SCR-2 α -silicon

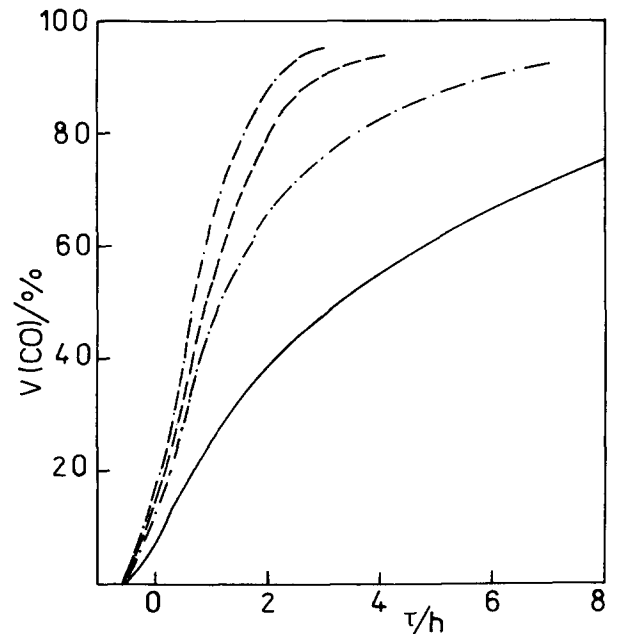


Fig. 8. Evolution of silica reduction expressed in vol.% of total amount of CO evolved (details the same as in Fig. 7). Mass % of SCR-2 seeds: (—) 0, (---) 5, (· · ·) 10 and (- · - ·) 20.

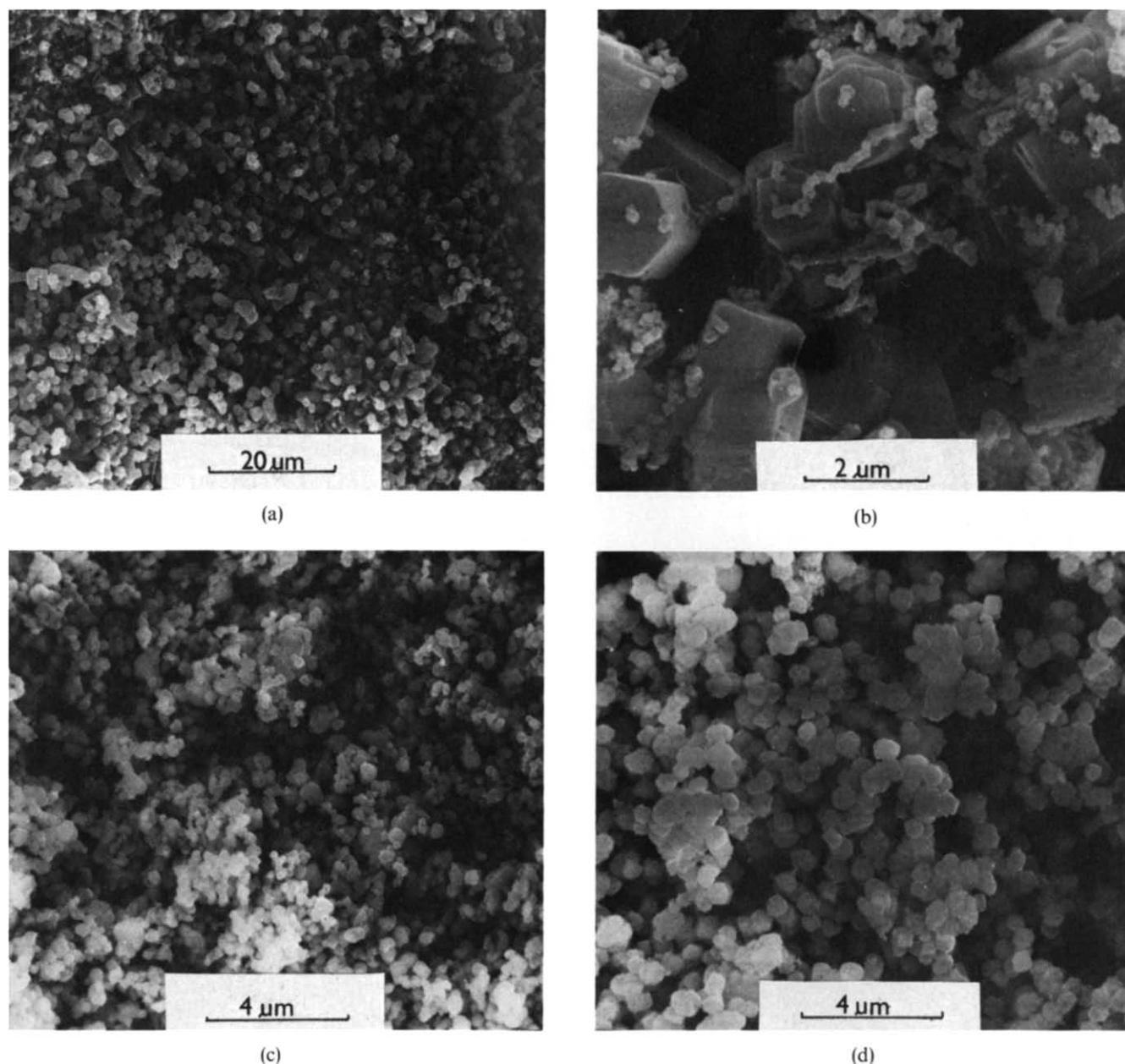


Fig. 9. Morphology of some typical α -silicon nitride powders prepared by carbothermal reduction and nitriding of silica: (a) without seeding, (b) 10 mass% of fine silicon added (small grains are most probably β -SiC crystals), (c) 10 mass% of SCR-2 seeds added and (d) 5 mass% of seeds and controlled silicon monoxide evolution.

nitride crystals on the morphology of the products is documented in Fig. 9. Without seeding coarse 2–4 μm α -silicon nitride crystals were obtained (Fig. 9(a)). With 10 mass% of seeds particle sizes are reduced to about 0.2–0.7 μm (Fig. 9(c)). The narrow particle size distribution in Fig. 9(d) was obtained in experiments under favourable conditions with 5 mass% of seeds and with a controlled rate of silicon monoxide evolution, where spontaneous nucleation was probably suppressed.

4.3 Effect of temperature

As was shown in Section 2, thermodynamic calculations indicate that silicon carbide rather than

silicon nitride should be formed in the $\text{SiO}_2\text{-C-Si}_3\text{N}_4\text{-N}_2$ system above 1450°C. However, numerous published, and also our own previous, results contradict this fact. One of the reasons why silicon nitride can be currently prepared at 1510°C was proposed above (i.e. the activity of carbon near silicon nitride grains can be lower than unity). Another reason can be that some of the used thermodynamic data (standard Gibbs energies of formation of some substances in question) are not exact. We tried to contribute to the elucidation of the questions in the following experiments. Data on these are summarised in Table 5.

Aerosil–acetylene carbon black mixtures seeded

Table 5. Data on experiments, chemical and phase compositions of products

Number ^a	Temperature (°C)	N ₂ flow (dm ³ /h)	Time (h)	Content ^a (mass%)			Phase composition ^b (mass%)		
				N	C	O	Si ₃ N ₄ total	SiC	SiO ₂
14	1 550	20	2.0	35.2	1.1	4.3	88	4	8
15	1 590	30	1.5	10.8	20.7	2.7	27	68	5
16	1 510	15	4.0	36.8	0.6	3.3	92	2	6
17	1 550	15	4.0	26.6	7.7	3.0	67	27	6

^a Starting mixtures: numbers 14 and 15—Aerosil + acetylene black (1:1 by mass) seeded with 10% of SCR-2; numbers 16 and 17—60% α -Si₃N₄ + 40% acetylene black (product prepared according to experiment number 4, pressed and crushed).

^b After free carbon burning-out.

^c Calculated from chemical analyses after free carbon burning-out.

with 10 mass% of SCR-2 silicon nitride were used as starting mixtures in experiment numbers 14 and 15. At $1550 \pm 10^\circ\text{C}$ (number 14) α -silicon nitride was the dominant product and only traces of β -silicon nitride and β -silicon carbide were found by X-ray diffraction. At $1590 \pm 10^\circ\text{C}$ (number 15) β -silicon carbide was predominantly formed by the reaction and the portion of silicon nitride in the product corresponded to the amount added into the starting mixture (note that phase compositions in Table 5 are given for samples after free carbon burning out).

Kinetics of silicon nitride formation at 1510 and 1550°C are compared in Fig. 10.

For experiments numbers 16 and 17 the green products prepared in the same way as number 4 (Table 2) served as starting mixtures. The mixtures consisted of about 60 mass% of α -silicon nitride and of about 40% of acetylene carbon black. The as-prepared mixtures were cold pressed and subsequently crushed, and the procedure was repeated three times to obtain the most intimate contact

between the silicon nitride and carbon grains. The crushed mixtures were then heated at $1510 \pm 10^\circ\text{C}$ (number 16) and at $1550 \pm 10^\circ\text{C}$ (number 17) for 4 h in a nitrogen flow similar to the synthesis procedures. Practically no changes in the chemical and phase compositions were observed in the mixture heated at 1510°C. The mixture heated at 1550°C was significantly changed, and after carbon burning-out the product consisted of about 70 mass% of silicon nitride and of about 25% of β -silicon carbide. The portion of β -silicon nitride was slightly increased to about 8%.

The above results indicate the following:

- The temperature at which the standard Gibbs energy of reaction (5) at 101 kPa N₂ is equal to zero is shifted above 1440°C. It probably falls within the interval 1510–1550°C.
- It is reasonable to assume that in carbothermal reduction and nitriding of silica silicon nitride is formed in sites where activity of carbon is lower than unity. Therefore silicon nitride formation is possible up to about 1550°C, when a sufficient supply of nitrogen and an efficient removal of carbon monoxide are secured. It is obvious that these presumptions apply only for high-purity reaction systems.

5 Conclusions

Reaction of high-purity silica and carbon in nitrogen flow begins at approximately 1250°C and practically pure α -silicon nitride is formed up to $1550 \pm 10^\circ\text{C}$.

Kinetics of the reaction is accelerated by seeding with a fine silicon nitride powder and the intensity of the seeding effect increases with increasing surface area of the seeding powder. The appropriate seeding and control of silicon monoxide evolution results in highly uniform and isometric α -silicon nitride

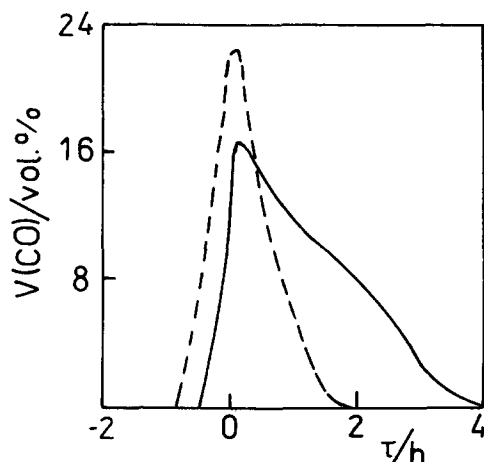


Fig. 10. Actual concentrations of CO in outlet gases at carbothermal reduction and nitriding of silica (Aerosil + acetylene black mixture seeded with 10 mass% of SCR-2): (—) 1510°C, 250 cm³/min of N₂, and (---) 1550°C, 330 cm³/min of N₂.

crystals. An addition of free silicon to the reaction system promotes β -silicon carbide formation.

Silicon monoxide evolved in the early stages of the reaction must be effectively consumed for silicon nitride growth. If not, its reoxidation, and thus the redistribution of silica in the reaction mixture, occurs. Such heterogeneities, formed during the reaction, significantly slow down the overall process.

The equilibrium temperature of the reaction $\text{Si}_3\text{N}_4 + 3\text{C} \rightleftharpoons 3\text{SiC} + 2\text{N}_2$ at 101 kPa N_2 was found to fall within the interval of $1510 \pm 10^\circ\text{C}$ to $1550 \pm 10^\circ\text{C}$.

Since formation of α -silicon nitride at 1550°C was proved and its thermodynamic instability at this temperature was found, it was concluded that silicon nitride is formed in the sites where carbon activity is lower than unity. Surfaces of α -cristobalite grains, formed during the reaction, were found to serve for the nucleation and growth of silicon nitride crystals. Different mechanisms of silicon nitride formation at 1550°C and at lower temperatures are not expected, therefore it is assumed that the above conclusion is valid also for temperatures lower than 1550°C .

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