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Control of particle size in Si_3N_4 powders prepared by high-pressure carbothermal nitridation

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The grain size variation in "unseeded" Si_3N_4 powders, prepared by high-pressure carbothermal nitridation of SiO_2 (in stoichiometric 1 : 2 proportions with C), has been studied by means of scanning electron microscopy (SEM) and "Sedigraph" measurements. The size is a function of process parameters, of which the reactant surface area was found to be the most important. Specifically, with an SiO_2 area $A(SiO_2) \approx 50\ m^2\ g^{-1}$ in the reaction mixture, the resulting mean Si_3N_4 particle diameter, $d(Si_3N_4)$, is very sensitive to the carbon surface area, $A(C)$, such that the minimum $d(Si_3N_4) \approx 1\ \mu m$ was obtained with $A(C) = 30 m^2\ g^{-1}$ and the maximum $d(Si_3N_4) \approx 7\ \mu m$ with $A(C) = 115\ m^2 g^{-1}$. Using mixtures with $A(SiO_2) = 50\ m^2 g^{-1}$ and $A(C) = 115\ m^2 g^{-1}$, a slight dependence of $d(Si_3N_4)$ on the furnace heating rate was also observed; larger grains ($\approx 7\ \mu m$) were obtained with 20 deg min^{-1} than with 2 deg min^{-1} ($\approx 5\ \mu m$).

The grain size was found to be virtually independent of nitrogen pressure (in the range 0.3–6.5 MPa), annealing temperature (1470–1830 °C) and gas flow rate (2–20 $l_{(stp)}\ min^{-1}$).

1. Introduction

Carbothermal reduction and simultaneous nitridation (CTN) of SiO_2 according to

$$3SiO_{2(s)} + 6C_{(s)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} + 6CO_{(g)} \quad (1)$$

is a preparation method for Si_3N_4, generally recognized to produce powders with a narrow particle size distribution and high yield of the desirable α modification [1–3]. "Seeding", i.e. addition of small amounts of fine Si_3N_4 powder to the $C + SiO_2$ starting mix, has been a common procedure to reduce the final particle size to below 1 μm.

At this Laboratory, various aspects of Si_3N_4 powder preparation by CTN at *elevated* nitrogen pressures have been studied [4, 5]. Use of even a moderately high $pN_2 \sim 2$ MPa makes it possible to perform the carbothermal synthesis at high temperatures ~1800 °C without concurrent SiC formation [6], which occurs above ca. 1500 °C at atmospheric pressure. Furthermore, the irreversible losses of SiO(g) from the sample, which may be substantial at 0.1 MPa, have been found to be much reduced on a pressure increase to ca. 2 MPa. These advantages enable the use of *stoichiometric* $C + SiO_2$ charges (2:1) in high pressure (HP)-CTN at high temperatures, while still maintaining low oxygen and carbon impurity levels. This is required in order to avoid an oxidation step, needed to remove the extra carbon in Si_3N_4 powders prepared at atmospheric pressure, as a carbon excess is normally required to improve the kinetics in the permissible temperature range < 1500 °C.

The present work is a systematic study of the variation in Si_3N_4 particle size as a function of process parameters in HP-CTN, using unseeded, stoichiometric charges. The purpose was to identify other important factors for grain size control than just seeding. We believe that ceramics technology could benefit from increased knowledge in this field.

2. Previous studies on CTN-Si_3N_4 particle morphology

Si_3N_4 crystals mainly appear in two forms in powder synthesis; either as whiskers (fibres, narrow blades), which easily grow to centimetre lengths and with high aspect ratios, or as microscopic, short columnar grains (occasionally reduced to platelets) with hexagonal cross-sections. Generally, whiskers produced in synthesis experiments with pure C and SiO_2 seem to be α-Si_3N_4, although formation of β-phase whiskers has been reported [7].

At high temperatures, $\geqslant$ 1400 °C, gas species such as SiO are generally believed to be involved in the

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Si_3N_4 formation, e.g. according to

$$3SiO_{(g)} + 3CO_{(g)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} + 3CO_{2(g)} \qquad (2)$$

Whether needles or columns will form is suggested to be essentially a matter of charge geometry [7, 8]. It is also to some extent due to the choice of process parameters affecting the degree of supersaturation of species such as $SiO_{(g)}$ [9].

Efforts to optimize the Si_3N_4 synthesis have focused on the nearly equiaxed columnar grains, as these are more attractive than fibres as a precursor material for structural ceramics. Control of particle morphology in CTN is a subject addressed in several papers. Until now, no generally accepted theory for nucleation, growth and size control of Si_3N_4 grains has been formulated, based on the different observations and conclusions made so far. "Seeding" of the $C + SiO_2$ starting mix with ~5% fine-grained Si_3N_4 powder is effective for grain size control, as was first demonstrated by Inoue *et al.* [10]. Observations such as those of Shanker *et al.* [7], that the final particle size in a batch approached the size of the seeds with increasing seed content, support the view that the added Si_3N_4 grains are real seeds, constituting nuclei for continued growth. It should be noted, though, that a 5 wt% addition of a very coarse-grained seeding material (~5μm) was also found to be an efficient grain-refiner, producing a submicrometre powder [11]. This suggests that existing Si_3N_4 *surfaces* provide starting points for "cascade growth" of fresh crystals, to which the main seeding action should be ascribed. *Any* surface is not effective to this end. This was demonstrated [11] by a seeding experiment with fine BN powder, which turned out to have no grain-refining ability whatsoever.

Some factors reported to influence the Si_3N_4 grain size in unseeded powders are: temperature, reaction time and nitrogen gas flow rate [3], precursor preparation procedure [12] and carbon excess in the starting mix [13]. Zhang and Cannon have performed a systematic study [14, 15] of the nitridation kinetics and particle morphology of Si_3N_4, prepared from unseeded $C + SiO_2$ mixtures at 1400 °C in flowing nitrogen (101 kPa). Starting materials from different sources were used, and in different proportions ($C/SiO_2 = 3.5$–16). The SiO_2 and C surface areas were varied in the range 50–238 and 34–680 $m^2 g^{-1}$, respectively. The Si_3N_4 particle diameter was found to range from 1 to 7 μm; the minimum size obtained with combinations of either high C or high SiO_2 surface area.

3. Experimental procedure

Quartz (q and Q), amorphous silica (s and S) and carbon black (c and C) powders were used as starting materials (upper and lower case letters designate the relative sizes of the reactant particles). The solids are specified in Table I. The nitrogen gas with impurities $O_2 < 5$ p.p.m. and $H_2O < 5$ p.p.m., was used without further purification. Gas mixtures of $CO + N_2$ of the same purity were used in some comparison experiments.

Starting mixtures were seven combinations of the silica/quartz and carbon-black powders, in stochiometric proportions according to the overall reaction (Reaction 1). The powder mixtures were homogenized by rolling in an ethanol slurry with Sialon milling balls for 4 days. They were then pre-dried to a plastic mass and extruded to granules (diameter = 1.5 mm, length = 1–6 mm), which were further dried to remove the alcohol prior to charging.

The carbothermal reduction was performed in a gas autoclave with a vertical graphite furnace described earlier [4, 9]. Approximately 0.4 g granules were spread on a perforated graphite foil in the sample holder. The autoclave was flushed three times with nitrogen (1 MPa) at room temperature and three times during heating (below 600 °C). Nitrogen gas was forced through the charge and then the shortest way

TABLE I Specification of C and SiO_2 starting materials

Symbol	Reactant	Grain size	BET surface ($m^2 g^{-1}$)	Main impurities	Source, grade
q	Quartz	< 34 μm	1	99.8% pure	p.a., E. Merck Gmbh
Q	Quartz	< 100 μm	0.3	99.8% pure	p.a., E. Merck Gmbh
s	Amorphous SiO_2	12 nm	200	99.8% SiO_2, $Al_2O_3 <$ 0.08%, $TiO_2 <$ 0.03%	Aerosil, Degussa A.G.,
S	Amorphous SiO_2	40 nm	50	99.8% SiO_2, $Al_2O_3 <$ 0.08%, $TiO_2 <$ 0.03%	Aerosil, Degussa A.G.,
c	Carbon black	20 nm	115	H < 6%, S, O, N < 1%	Nordisk Philblack Co., N220
C	Carbon black	70 nm	30	H < 6%, S, O, N < 1%	Nordisk Philblack Co., N774

BET, Brunauer–Emmett–Teller.

out via a reducing valve and a flowmeter. The gas flow rate (Φ) and the pressure (p) in the experiments varied in the ranges 1.6–20 $l_{(stp)}\,min^{-1}$ and 0.3–6.5 MPa, respectively. The temperature was measured with a (W-W,Re) thermocouple, calibrated against the melting points of gold, palladium and platinum. The maximum deviation of the measured temperature from the actual value was found to be ± 5 deg, while the plateau temperature could be held within ± 1 deg. The temperature programme was controlled by a computer system. Different heating rates were used, but the cooling rate was normally 30 deg min^{-1}. The gas outlet valve was usually opened at 1200 °C on heating and closed at 1300 °C after annealing.

The product phases (Si_3N_4) were checked by X-ray powder diffraction (XRD, Guinier–Hägg type focusing cameras), and the α/β ratios were determined by diffractometry. The particle size and morphology were characterized by scanning electron microscopy (SEM, a Jeol JSM-820 instrument) on as-received powders. The particle size distribution of some samples were measured with a "Sedigraph" instrument.

4. Results

4.1. Charges with coarse SiO_2

CTN with the relatively coarse-grained quartz powder (1 $m^2\,g^{-1}$) as starting material always resulted in an Si_3N_4 mean particle size $\leqslant 2\ \mu m$, as judged from SEM pictures (Fig. 1). The synthesis parameters that were varied are temperature, pressure, gas flow rate and heating rate, as listed in Table II.

The effect of an increased CO content (1%) in the reaction gas during heating-up to the plateau temperature was studied in experiment no. 10. Under such conditions nitridation is hampered, compared with a run in pure nitrogen; 3.7 wt % C remained in the sample after one hour. Also run no. 1 at relatively low temperature and with a very coarse-grained quartz (0.3 $m^2\,g^{-1}$) had a poor yield of Si_3N_4, leaving 18% C and 22 wt % O. Sample no. 2 with a coarse-grained carbon (30 $m^2\,g^{-1}$) had 5.3 wt % and 1.4 wt % residual C and O, respectively. All other runs with one or two hours' annealing produced powders with residual C amounts < 3 wt %.

The short run no. 4; mere heating to 1550 °C and then immediate cooling at a fast rate, 30–40 deg min^{-1}, produced no Si_3N_4 in the interior of the granule, but the short run no. 5 to 1680 °C did; small columnar crystals ($< 2\ \mu m$) were observed in SEM, together with whiskers from the granule surface. (Fig. 1(b)).

The estimated relative amount of the α-modification is given for most runs in the Table. It is related to the gas velocity and the heating rate in a manner observed and discussed before [4, 9]. Formation of the metastable α-phase is generally favoured by a rapid heating and a moderate gas velocity (i.e. low flow rate and relatively high pressure), which may be indicative of a rapid nucleation under these conditions. This subject will be further touched upon in the Section 5.

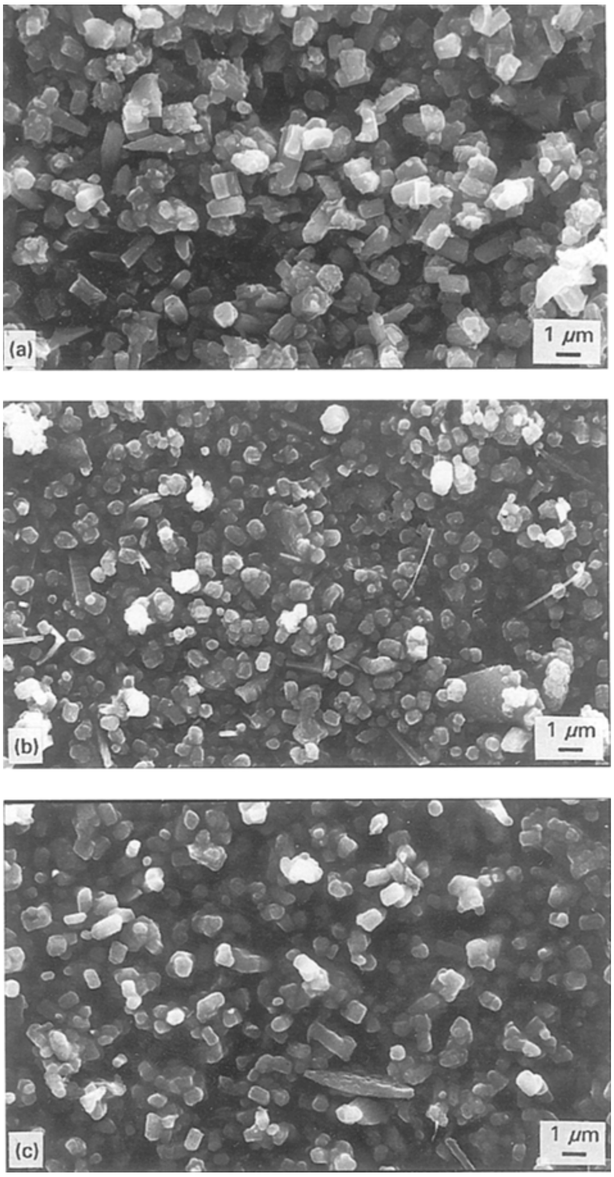


Figure 1 SEM photos of various product powders, with quartz as SiO_2 reagent. (a) Sample (as-received) from run no. 3 at 1550 °C with a "c + q" starting mixture. (b) Sample from a short-time run (no. 5) to 1680 °C. Unreacted carbon has been burnt off in air at 600 °C. Whiskers and small equiaxed grains of Si_3N_4 are seen as well as unreacted quartz. (c) Sample (as-received) from run no. 8 with "c + q" at 1830 °C. A piece of a whisker is seen among the columnar grains.

4.2. Charges with fine-grained SiO_2

Of the four combinations of carbon and silica tried; "c" and "C" with "s" and "S", the one with the finest carbon but not the finest silica, "c + S", was found to produce the largest Si_3N_4 particles, up to 7 μm (Fig. 2). The results of variation of the synthesis parameters are presented in Table III. As can be seen, neither the pressure nor the gas flow rate, in the ranges 2–6.5 MPa, 2–20 l min^{-1}, had any influence on the mean particle size, $d(Si_3N_4)$. Annealing at 1550 or 1830 °C did not make any difference, but evidently somewhat larger Si_3N_4 grains were obtained on fast heating, $\geqslant 10$ deg min^{-1}, than by heating at 2 deg min^{-1} over the anticipated nucleation range 1500–1600 °C (cf. nos. 14–17). This difference (7 versus 5 μm) is seen to hold for the columnar crystals in the

TABLE II Results of CTN runs with quartz as SiO_2 reagent. Particle size figures are the maximum grain length, as estimated from SEM pictures

Run no.	Starting materials	Temperature T (°C), $\Delta T/\Delta t$ (°C min^{-1}), t(h)	p N_2 (MPa)	$\Phi(N_2)$ (l min^{-1})	$\alpha/\alpha+\beta$ (%)	Particle size (μm)
1	c + Q	1470 20 ↗ 2	0.7	11	100	< 2
2	C + q	1550 20 ↗ 2	0.3	1.6	91	< 2
3	c + q	1550 20 ↗ 2	0.3	1.7	89	< 2 (Fig. 1(a))
4	c + q	1550 20 ↗ 0	1.5	1.8	-	No Si_3N_4
5	c + q	1680 20 ↗ 0	1.5	1.7	-	< 1 (Fig. 1(b))
6	c + q	1680 20 ↗ 1	1.5	4	92	< 2
7	c + q	1830 2 ↗ 1	2.5	1.8	73	< 2
8	c + q	1830 10 ↗ 1	2.6	1.9	81	< 2 (Fig. 1(c))
9	c + q	1830 10 ↗ 1	1.5	11	51	< 2
10	c + q	1830 (N_2 + 1 % CO) 10 ↗ 1	1.5	11/1.9	59	< 2

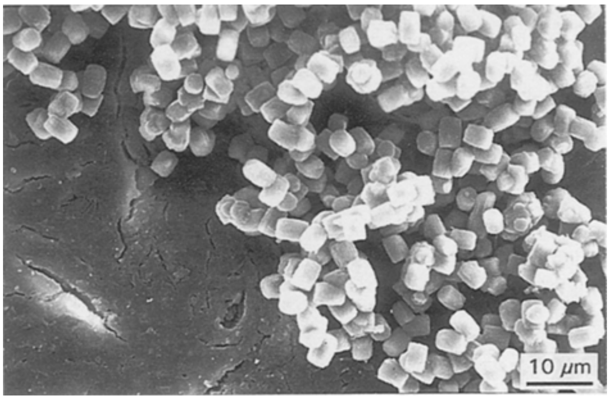


Figure 2 SEM photo of sample (as-received) from run no. 11 with "c + S" at 1830 °C, $\Delta T/\Delta t = 2$ deg min^{-1}.

SEM pictures (Fig. 3(a–d)) and is also reflected in the Sedigraph data; the distribution curves (Fig. 4) and mean particle size values constituting more objective measures.

Interestingly, the combination of coarse carbon "C" with "S" yielded the finest powder, ~ 1 μm (Fig. 3(g,h) and 5). The combinations "C + s" and "c + s" produced an intermediate grain size of ~ 3 μm (Fig. 3(f)).

Run no. 18 was another test with CO (2%) mixed with the nitrogen, which had no influence on $d(Si_3N_4)$.

A comparison of samples nos. 19, 22 and 24 (Fig. 3(g,h)) shows that no substantial particle growth was induced by prolonged annealing. Neither did a change of temperature programme, as in run no. 23, affect $d(Si_3N_4)$.

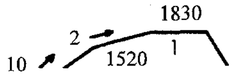
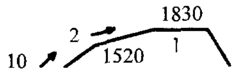
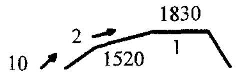
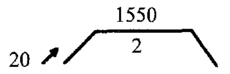
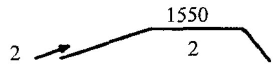
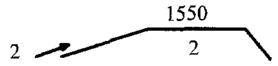
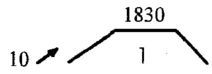
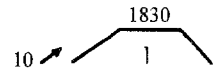
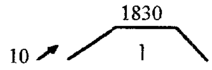
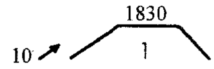
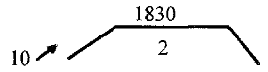
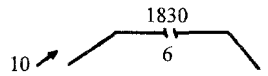
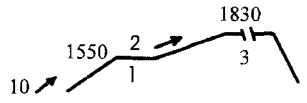
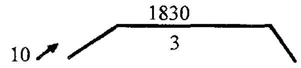
On comparing, by means of SEM, the products from repeated runs with different batches of the mixtures in Tables II and III, small discrepancies were in some cases revealed. The differences and trends pointed out here, which depend on the particular choice of parameters, are nevertheless significant.

Fig. 6 is a schematic diagram showing Si_3N_4 particle size as a function of C and SiO_2 surface area. Also included for comparison are the results of Zhang and Cannon [14].

5. Discussion

The very uniform Si_3N_4 grain size observed is indicative of a rapid nucleation on a large number of sites, from an SiO(g) supersaturated nitrogen gas. This was described by Zhang and Cannon as a "burst" of nucleation followed by growth [14]. Previous studies have demonstrated [16] that Si_3N_4 crystals grown from SiO(g) supersaturated $N_2(g)$ and CO + $N_2(g)$ were attached to available surfaces, i.e. nucleation is best described as heterogeneous. It must be stressed,

TABLE III Results of CTN runs with amorphous silica as starting material

Run no.	Starting materials	Temperature programme T (°C), $\Delta T/t$ (°C min^{-1}), t(h)	p N_2 (MPa)	$\Phi(N_2)$ (l min^{-1})	$\alpha/\alpha+\beta$ (%)	Particle size (μm)	
11	c + S		2.5	20	82	< 5	(Fig. 2)
12	c + S		6.5	20	100	< 5	
13	c + S		2.5	1.8	100	< 5	
14	c + S		2.0	20	–	< 7 (6.8)[a]	Fig. 3(a)) (Fig. 4)
15	c + S		2.0	20	–	< 5 (4.9)[a]	(Fig. 3(b)) (Fig. 4)
16	c + S		6.0	20	–	< 5 (4.7)[a]	(Fig. 3(c)) (Fig. 4)
17	c + S		2.5	20	–	< 7 (5.6)[a]	(Fig. 3(d)) (Fig. 5)
18	c + S	 (N_2 + 2% CO on heating)	2.5	2/20	–	< 7	(Fig. 3(e))
19	C + S		2.5	20	–	< 1 (1.9)[a]	(Fig. 5)
20	c + s		2.5	20	–	< 3	(Fig. 3(f))
21	C + s		2.5	20/5	–	< 3	
22	C + S		2.5	5/2	100	< 1	(Fig. 3(g))
23	C + S		2.5	5	–	< 1	
24	C + S		2.5	5	–	< 1	(Fig. 3(h))

[a] Mean particle size calculated by the Sedigraph method.

though, that no preferred substrate material was found; the Si_3N_4 crystals were observed to grow on SiO_2, Al_2O_3, BN, Mo and C. However, under specific conditions (a high CO content in the reactor, see below) Si_3N_4 precipitation tends to occur close to a reducing agent such as a carbon surface.

Evidently, supply of the majority reactant N_2, was not a restrictive factor in the experiments listed in Tables II and III, as the same mean particle size was obtained with pN_2 and $\Phi(N_2)$ varied over wide ranges. Instead the SiO(g) activity in the powder bed is likely to be a crucial parameter, governing the nucleation and growth rates (R_N and R_G). This is inferred from the fact that the SiO_2 surface area and (to some extent) also the heating rate influence the Si_3N_4 grain size. However, as $d(Si_3N_4)$ was found to be independent of the plateau temperature (between 1470 and 1830 °C), and because the temperature dependencies of R_N and R_G most certainly are different, the nucleation point on heating cannot be determined by pSiO. The observation that Si_3N_4 crystals did not appear in C + SiO_2 mixtures, according to SEM, until after the maximum in CO(g) evolution suggests that the parameter determining the nucleation point is p(CO). The analysed nitrogen content of the sample from a run such as no. 4, terminated before the CO maximum, was only 16% of that of a fully reacted sample [9]. This nitrogen is supposed to stem exclusively from

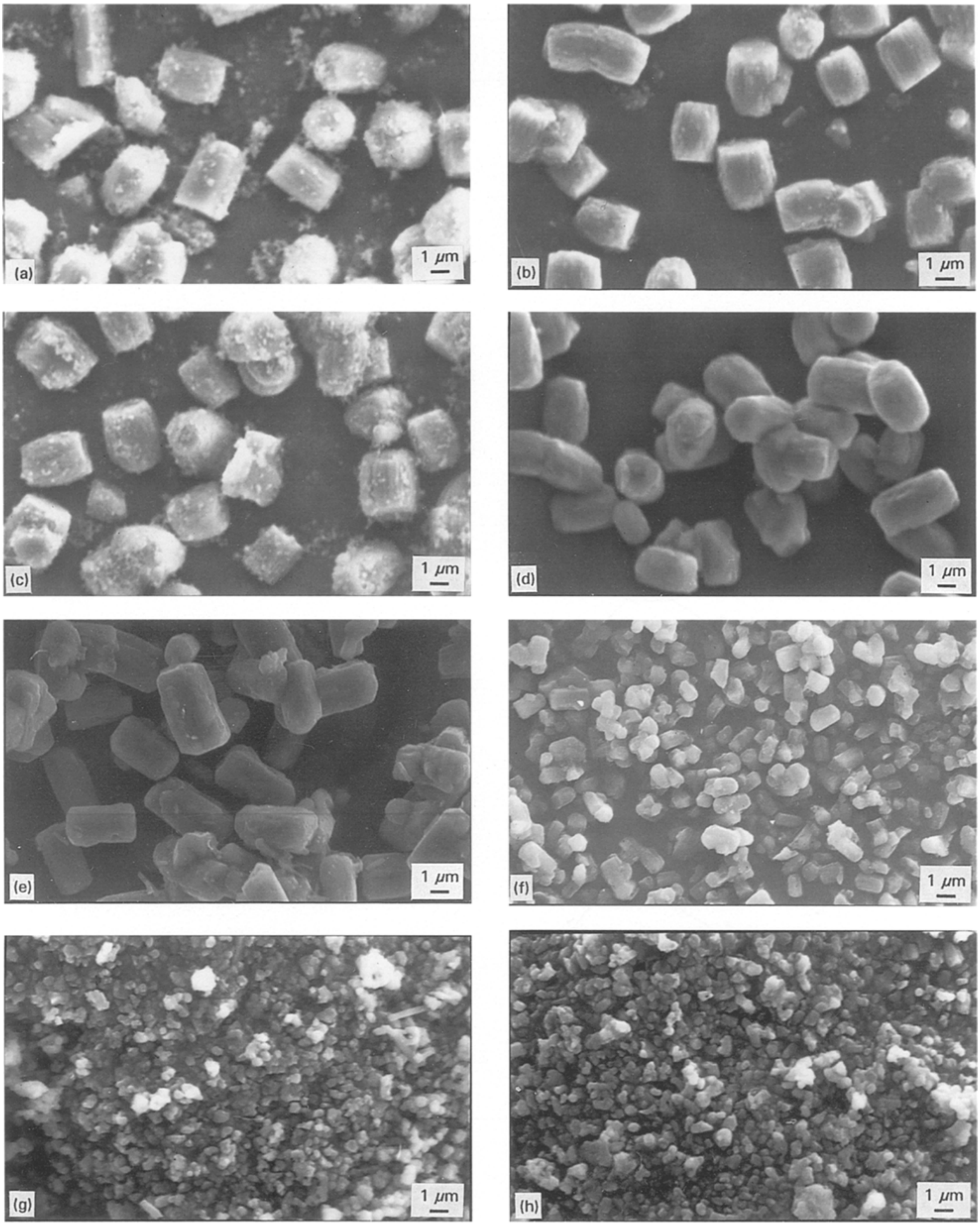


Figure 3 SEM photos of various product powders, with amorphous silica as starting material. (a) Sample (as-received) from run no. 14 with "c + S" at 1550 °C. The fine-fraction seen is unreacted carbon and silica. (b) Sample (as-received) from run no. 15 with "c + S" at 1550 °C, $\Delta T/\Delta t = 2\,\mathrm{deg\,min^{-1}}$. (c) Sample (as-received) from run no. 16 with "c + S" at 1550 °C, 6 MPa. The fine-fraction seen is unreacted carbon and silica. (d) Sample (as-received) from run no. 17 with "c + S" at 1830 °C. (e) Sample (as-received) from run no. 18 with "c + S" at 1830 °C in N_2 + 2% CO. (f) Sample (as-received) from run no. 20 with "c + s" at 1830 °C. (g) Sample (as-received) from run no. 22 with "C + S" at 1830 °C, 6 h. (h) Sample (as-received) from run no. 24 with "C + S" at 1830 °C, 3 h.

α-Si_3N_4 whiskers formed on the granule surfaces, i.e. grown in almost pure N_2. It has been proved by means of differential scanning calorimetry (DSC) [9] that the SiO_2 starting material (quartz) in such a run is to a high degree (> 50%) transformed into amorphous silica. Such a change should be mediated by SiO(g), and evidently a high pSiO is not sufficient for Si_3N_4 nucleation. In sample no. 5, on the other hand, collected after passing the CO maximum, the N content was 59% of that in pure Si_3N_4, and small crystals of

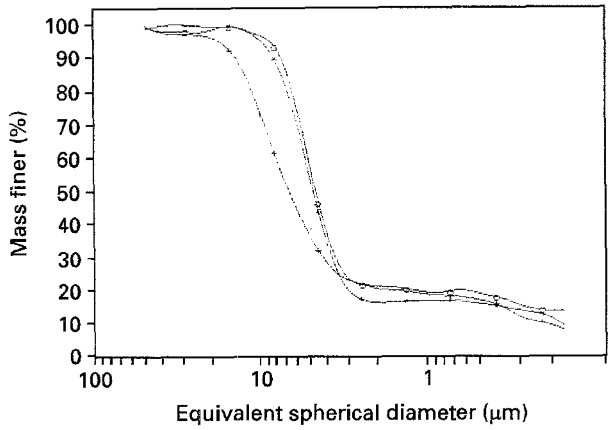


Figure 4 Particle size distribution curves for powder samples from runs nos. 14 (+), 15 (*) and 16 (□), determined with the Sedigraph instrument. An appreciable fine-fraction, < 2 μm, is seen, probably consisting of unreacted carbon and silica particles.

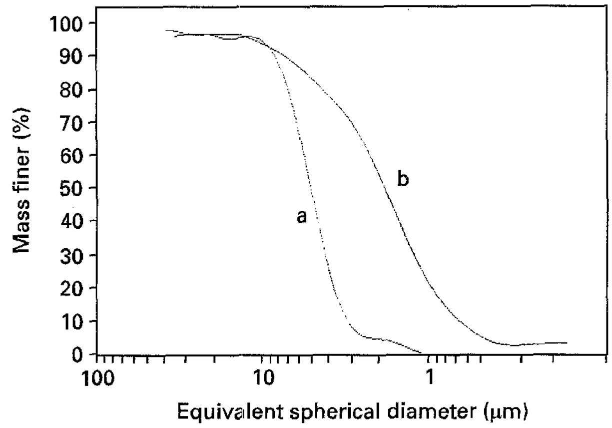


Figure 5 Sedigraph curves from samples nos. 17 (a) and 19 (b).

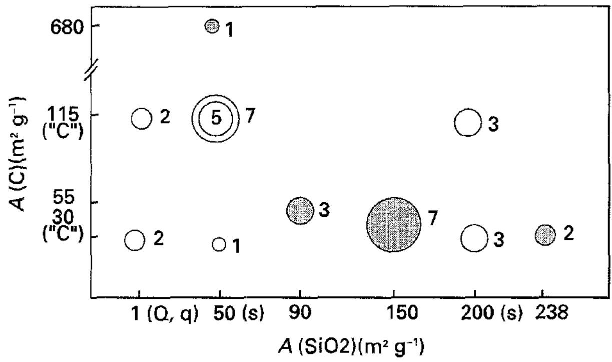


Figure 6 Schematic diagram showing the obtained Si_3N_4 particle size as a function of surface area of the C and SiO_2 starting materials. Also included (hatched circles) are the results of Zhang and Cannon [14]. The outer circle in the double symbol is the particle size obtained at $\Delta T/\Delta t = 20\,\mathrm{deg\,min^{-1}}$, the inner circle at $\Delta T/\Delta t = 2\,\mathrm{deg\,min^{-1}}$.

this phase are clearly seen in the interior of the sample in SEM photos (Fig. 1(b)).

The existence of a pCO threshold for Si_3N_4 formation in CTN is well established by previous investigators. Zhang and Cannon [14, 15] calculated a limiting value of 23 kPa at 1400 °C and 100 kPa total pressure, based on the equilibrium constants for the reactions

$$3SiO_{(g)} + 3CO_{(g)} + 2N_{2(g)} \rightarrow Si_3N_4 + 3CO_{2(g)} \quad (2)$$

$$SiO_2 + CO_{(g)} \rightarrow SiO_{(g)} + CO_{2(g)} \quad (3)$$

$$3SiO_{(g)} + 3C + 2N_{2(g)} \rightarrow Si_3N_4 + CO_{(g)} \quad (4)$$

and

$$CO_2(g) + C \rightarrow 2CO(g) \quad (5)$$

They also sketched a probable reaction scheme involving initial nucleation of Si_3N_4 according to Reactions 3 and 4, followed by growth according to Reactions 2 and 3, as a function of the fluctuating pCO during the course of a typical CTN synthesis. Ekelund and Forslund [16] preferred to regard the oxygen activity as the controlling parameter for Si_3N_4 formation. This quantity pO, the partial pressure sum of atomic and molecular oxygen, is regulated by the activities of a number of gas species, such as SiO, CO, CO_2 and NO. By means of the computer program SOLGASMIX [17] and JANAF thermochemical data [18], pO and pSiO at different temperatures and pressures (1510, 1620, 1730 °C, 0.5, 1.0, 3.0 MPa) were calculated for some crucial positions within a reaction mixture; e.g. next to the SiO_2 surface and the C surface. The calculations (with some simplifying assumptions) showed that the SiO(g)-generating reaction (Reaction 3) is stimulated by increases in temperature, nitrogen pressure and also CO(g) content in the gas. Formation of Si_3N_4 by gas phase routes ($SiO(g) + N_2(g)$), on the other hand, is hampered by increased temperature and CO content, but stimulated by increased pN_2. With a gas phase containing 1% CO and a temperature of 1510 °C, Si_3N_4 does not form at pressures lower than 0.5 MPa. At 1620 °C a nitrogen pressure of 1.0 MPa, and at 1730 °C 3.0 MPa, is required for formation of Si_3N_4 free of SiC in the same gas mixture. These calculated limits have been verified experimentally [16].

Runs nos. 10 and 18, with N_2 + CO gas mixtures, both produced Si_3N_4 albeit at a slower rate than without CO addition. Interestingly, in spite of the imposed pCO being close to the threshold values in these cases, it turned out to have no effect on the Si_3N_4 grain size and morphology (cf. runs nos. 9 and 17). This may reflect a balancing role played by pCO in maintaining the ratio of R_N to R_G. Such a balance may also be the reason why the grain size appears independent of the nitrogen pressure. Increased nitrogen pressure favours SiO(g) generation, as shown by thermodynamic calculations, but at the same time hampers Si_3N_4 formation by lowering the pCO threshold value.

The slight increase of Si_3N_4 size found when the heating rate was raised from 2 to 20 deg min^{-1} indicates that, even in case of a rapid "burst of nucleation", growth occurs to some extent in parallel, and R_G is somewhat enhanced relative to R_N by faster heating. The other possibility, that R_N is slowed down by faster heating, which should generate SiO(g) at a higher rate, is less likely. If we regard a high content of the metastable α-modification as indicative of a rapid nucleation of Si_3N_4, the conclusion is that the difference in R_N between runs such as nos. 8 and 9 and 11 and 13 is compensated by R_G to produce the same final $d(Si_3N_4)$.

If a high SiO(g) evaporation rate leads to a large $d(Si_3N_4)$ one should expect large particles from a high-surface area SiO_2 starting material. The samples with $A(SiO_2) = 1$ and $200\ m^2\ g^{-1}$ were found to follow this trend (Fig. 6), but the runs with $50\ m^2\ g^{-1}$ are striking exceptions. Zhang and Cannon rather found the opposite trend in their data and obtained more fine-grained Si_3N_4 with larger SiO_2 surface area. A difficulty here is to know at a given moment the actual silica surface area, as this rapidly decreases with time. Zhang and Cannon noted an appreciable coarsening of the SiO_2 after short time at 1400 °C, and found the rate of SiO volatilization at this temperature to be about equal in samples having an initial $A(SiO_2) = 90$ and $238\ m^2\ g^{-1}$. As mentioned above, Ekelund and Forslund [9] established by means of DSC that the transformation rate of quartz to amorphous silica is surprisingly high in a $C + SiO_2$ mixture undergoing CTN. We also observed by SEM a drastic morphological change, during a run such as no. 4, of the originally sharp-edged quartz grains into spherical particles.

Hence, it is difficult to relate the resulting $d(Si_3N_4)$ to the *initial* $A(SiO_2)$, as the SiO(g)-generation at every stage of the process, specifically the nucleation point, will depend on the *actual* $A(SiO_2)$, which rapidly changes with time. The rate of change will depend on the type of silica, and also on pO, i.e. the reducing capacity of the carbon reagent, which affects the rate of SiO_2 dissociation. Carbon surface area and C/SiO_2 ratio have been recognized by previous investigators as important parameters for control of Si_3N_4 grain size. Zhang and Cannon obtained a minimum $d(Si_3N_4)$ with the highest $A(C) \sim 680\ m^2\ g^{-1}$, an effect that they ascribed to the proposed role of the carbon surface as providing nucleation sites for Si_3N_4. Accordingly, a high C/SiO_2 ratio should have the very minimizing effect on $d(Si_3N_4)$, that has actually been observed [13, 14].

Our data from runs with stoichiometric charges ($C/SiO_2 = 2.0$) display an irregular variation, which we cannot explain by any simple model. It may well be that in a charge without carbon excess the local pSiO and pO, governing R_N and R_G, become very sensitive to the microscopic geometry of the charge (C and SiO_2 grain size). This seems particularly to be the case for silica surface areas around $50\ m^2 g^{-1}$. The difference in $d(Si_3N_4)$ obtained with different combinations of SiO_2 and C starting materials should thus be a result of small perturbations of a delicate balance between SiO(g) generating processes, reactions controlling the oxidation potential, Si_3N_4 nucleation and growth reactions, as well as various transport processes (gas diffusion).

Great care was taken in performing the sample preparation procedure; mixing, homogenization and granulation, in the same strictly reproducible manner for each batch in this study. Even so, there is still a possibility that the differences in $d(Si_3N_4)$ obtained were to some extent due to differences in C and SiO_2 distribution uniformity or granule density. Zhang and Cannon, using carbon excess in their mixtures, concluded that the synthesis results were very little dependent on mixing techniques (however also stressed the importance of a uniform reactant distribution). An exhaustive, systematic study to clarify this matter would in any case be useful.

6. Conclusions

1. By nitridation of mixtures of C and SiO_2 of ordinary commercial grade, Si_3N_4 powders with a mean grain size in the range 1 to 7 μm and with a narrow size distribution can be prepared in a controlled manner.
2. The reactant surface area is decisive for $d(Si_3N_4)$ in an unseeded powder. In particular for starting mixtures with $A(SiO_2)$ around $50\ m^2 g^{-1}$, the resulting $d(Si_3N_4)$ is sensitive to the surface area of the carbon reactant.
3. The resulting $d(Si_3N_4)$ is independent of nitrogen pressure, gas flow rate, and synthesis temperature in the range 1470–1830 °C. No grain coarsening occurs even on 6 h annealing at high temperatures.
4. Some modulation of $d(Si_3N_4)$ by means of the heating rate is possible, such that slightly larger grains are obtained with a more rapid heating.

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References

1. A. HENDRY and K.H. JACK, in "Special ceramics 6", edited by P. Popper (British Ceramic Research Association, Stroke-on-Trent, England, 1975) p. 199.
2. K. KOMEYA and H. INOUE, *J. Mater. Sci.* **10** (1975) 1243.
3. S. NATANSOHN, in "Ceramic materials and components for engines", edited by V. J. Tennery (The American Ceramic Society, Westerville, OH, 1989) p. 27.
4. M. EKELUND and B. FORSLUND, *J. Amer. Ceram. Soc.* **75** (1992) 532.
5. M. EKELUND and B. FORSLUND, in "Ceramic powder science III", edited by G. L. Messing (The American Ceramic Society, Westerville, OH, 1990) p. 337.
6. T. JOHANSSON, U.S. Patent 4 530 825, 23 July 1985.
7. K. SHANKER, S. GRENIER and R. A. L. DREW, in "Ceramic powder science III", edited by G. L. Messing (The American Ceramic Society, Westerville, OH, 1990) p. 321.
8. I. A. RAHMAN and F. L. RILEY, *J. Eur. Ceram. Soc.* **5** (1989) 11.
9. M. EKELUND and B. FORSLUND, *ibid.* **9** (1992) 107.
10. H. INOUE, K. KOMEYA and A. TSUGE, *ibid.* **65** (1982) C-205.

11. M. EKELUND and B. FORSLUND, in Proceedings of the 4th International Symposium on Ceramic Materials and Components for Engines, June 1991, Gothenburg, Sweden, edited by R. Carlsson, T. Johansson and L. Kahlman (Elsevier, 1990) p. 196.
12. S. J. P. DURHAM, K. SHANKER and R. A. L. DREW, in "Production and processing of fine powders", edited by A. J. Plumpton (Pergamon Press, New York, 1988) p. 549.
13. V. FIGUSCH and T. LICKO, in "High tech ceramics", edited by P. Vincenzini (Elsevier, Amsterdam, 1987) p. 517.
14. S. C. ZHANG and W. R. CANNON, *J. Amer. Ceram. Soc.* **67** (1984) 691.
15. W. R. CANNON and S.-C. ZHANG, in "Ceramic materials and components for engines", edited by V. J. Tennery (The American Ceramic Society, Westerville, OH, 1989) p. 86.
16. M. EKELUND and B. FORSLUND, *J. Mater. Chem.* **2** (1992) 1079.
17. G. ERIKSSON, *Chemica Scripta* **8** (1975) 100.
18. JANAF Thermochemical Tables, edited by D. R. Stull and H. Prophet (NBS, Washington DC, 1971).

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