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Carbothermal Preparation of β-SiAlON Powder at Elevated Nitrogen Pressures

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Abstract

β-SiAlON powders have been prepared by carbothermal nitridation of kaolin or SiO_2 *plus* Al_2O_3 *mixtures at 1450-1800°C and elevated nitrogen pressures (1-50 bar). Powders with widely variable particle size and morphology were obtained depending on temperature, pressure, gas-flow rate, and raw-material type. An elevated nitrogen pressure effectively reduced SiO loss and suppressed SiC formation. Pure β-SiAlON powder of composition* $Si_{2.8}Al_{3.2}O_{3.2}N_{4.8}$ *and with a fine particle size (~1 μm) was produced at 1650°C, 50 bar* N_2 *and a high gas-flow rate for 2 h. The nitridation rate was hampered by an increase of the CO concentration in the system. © 1998 Elsevier Science Limited. All rights reserved*

Keywords: powders, solids state reaction, sialon, carbothermal reaction, nitrides.

1 Introduction

SiAlON ceramics ($Si_{6-z}Al_zO_zN_{8-z}$ with $z = 0–4$) are prepared by either reactive sintering of mixtures of Si_3N_4, Al_2O_3 and AlN powders or by sintering β-SiAlON powder. A possible advantage of this latter method would be better control of grain size and shape as well as of stoichiometry.

Lee and Cutler[1] were first to report carbothermal reduction and simultaneous nitridation (CTN) of a kaolin/carbon mixture, for instance according to:

$$\begin{aligned} &3Al_2Si_2O_5(OH)_4 + 15C + 5N_2(g) \rightarrow \\ &\rightarrow 2Si_3Al_3O_3N_5 + 15CO(g) + 6H_2O(g) \end{aligned} \quad (1)$$

Various aspects of this synthesis method for SiAlON powder have been studied by several investigators.[2–6] CTN has the potential of being an economical production process, utilizing inexpensive and abundant raw materials, but the task of preparing pure, monophasic β-SiAlON powder by this route is difficult. The main reason is that reaction (1) goes through a number of consecutive and parallel steps, which must proceed in the appropriate rate and order to yield the desired product. At the high synthesis temperature required, > 1400°C, appreciable amounts of SiO may be lost by irreversible evaporation from the sample, and thus change the Si/Al ratio in an uncontrolled manner during the synthesis.

In the present work, CTN syntheses of β-SiAlON powder was studied for powder mixtures of carbon/alumina/silica and carbon/kaolin, which were heated in nitrogen at *elevated pressure*. The purpose was to determine the effects of N_2 pressure, reaction time, temperature and nitrogen gas flow rate on reaction (1). Use of high pressure in CTN has been shown previously to be advantageous for preparation of Si_3N_4[7] and AlN powders.[8]

2 Previous Studies of β-SiAlON Preparation by CTN

Both natural aluminosilicate minerals and synthetic mixtures of SiO_2 plus Al_2O_3 have been used as starting materials in CTN experiments in flowing nitrogen at atmospheric pressure,[2–6,9] as reviewed by Cho and Charles.[10] A prerequisite for successful synthesis of such a complex compound as β-SiAlON is that the reactants are intimately mixed. Simple mechanical homogenization of Al- and Si- precursors seemed to be insufficient for preparation of a monophasic powder; mixing on an almost atomic scale rather, as in natural minerals and clays, was required. But even with sophisticated homogenization techniques, such as 'sol-gel' or intercalation of carbonaceous reactants into layer aluminosilicates,[11,12] control of the synthesis of pure β-SiAlON is difficult. It is likely to be accompanied by one or more of the other phases

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in the SiO_2-Al_2O_3-Si_3N_4-AlN system (Fig. 1), depending on which reaction path is followed.

A number of reaction steps have been identified or suggested for the most studied starting mixture; kaolin and carbon. Generally, after initial dehydration at $\leqslant$500°C, decomposition of kaolinite to mullite and silica is regarded as the first stage on heating:

$$3Si_2Al_2O_7 \rightarrow Al_6Si_2O_{13} + 4SiO_2 \qquad (2)$$

This step is independent of nitrogen concentration, as proved by Higgins and Hendry,[4] who concluded that this also holds for SiC formation at 1400–1500°C according to:

$$SiO_2 + 3C \rightarrow SiC + 2CO(g) \qquad (3)$$

β-SiAlON is subsequently formed by the reduction and nitridation of mullite with SiC, C and N_2 according to:

$$\begin{aligned} &Al_6Si_2O_{13} + 4SiC + 3C + 5N_2(g) \rightarrow \\ &\rightarrow 2Si_3Al_3O_3N_5 + 7CO(g) \end{aligned} \qquad (4)$$

The results of a recent NMR study by Mackenzie *et al.*[14] indicated, however, that Si-C bonds are formed relatively late in the reaction process to β-SiAlON, suggesting that reaction (3) is not the main SiC formation reaction.

As shown by thermodynamic calculations, appreciable partial pressures of SiO may build up over SiO_2 at T $\geq$1400°C. The excess SiO(g) swept from the sample by the gas flow can react with N_2 to form Si_3N_4 whiskers downstream on cooler parts of the furnace.

Cho and Charles[10] obtained a product mixture consisting of β-SiAlON, mullite, SiC, 15R and aluminium oxynitride $Al_{(64+x)/3}O_{(32-x)}N_x$, $0 \leq x \leq 8$ ('ALON'), when running a kaolin/carbon mixture, stoichiometric for reaction (1), for 2 h at 1400°C in flowing nitrogen (Φ = 1 l min^{-1}). At 1500°C, all other conditions being unchanged, the product phase assemblage was instead β-SiAlON, AlN and 15R. The relative amount of the 15R phase was much increased at the higher temperature, which was thought to be due to enhanced evaporation of SiO(g). They found the optimum reaction temperature to be 1450°C, yielding mainly β-SiAlON, and they also concluded that at higher temperature AlN forms from Al_2O_3, produced by decomposition of mullite and other aluminosilicate phases in the presence of carbon. Mixtures, substoichiometric with respect to carbon and run at 1450°C for 5 h produced, besides β-SiAlON, small amounts of X-phase (Fig. 1), Al_2O_3 and ALON. Hyperstoichiometric mixtures resulted in β-Si_3N_4 and AlN.

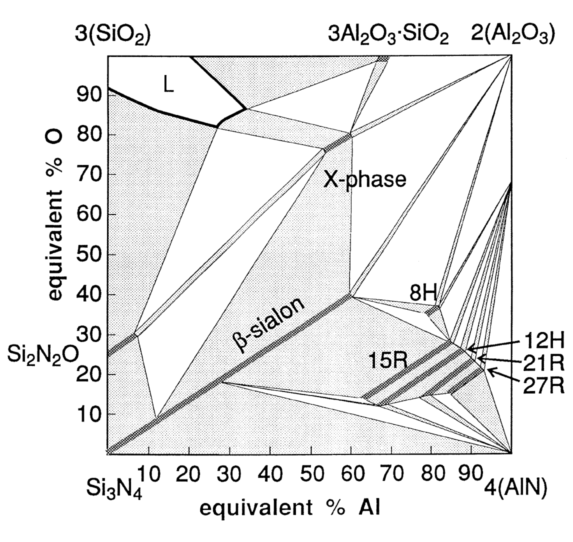


Fig. 1. The Si–Al–O–N behaviour diagram at temperatures of 1700–1730°C from Ekström and Nygren[13] and references therein.

The gas flow rate directly affects SiAlON synthesis, as it determines the supply of nitrogen reactant and also the extent of SiO(g) removal. Furthermore, it has an indirect effect as a regulator of the partial pressure of carbon monoxide in the sample space. Because this species appears on the product side of reactions such as (3) and (4), which have small equilibrium constants, it was found to exert a controlling action on the nitridation rate.[3,4] For rapid conversion CO(g) must be efficiently removed from the sample, but a flow rate in excess of the optimal for this task tended to shift the Al/Si ratio in an uncontrolled way, thereby producing for instance 15R together with β-SiAlON.[10,11]

Kokmeijer *et al.*[15] also found that, under conditions of constant flow, a critical pellet size d_c exists for each reaction temperature. Decreasing the diameter below this value has no influence on the reaction rate, while an increase above d_c reduces the rate. This is because pore diffusion of CO is rate determining in larger pellets, instead of the chemical reaction control below the critical size. At 1400°C d_c was found to be about 1 mm, and at 1500°C larger than 4 mm.

Cho and Charles[10] found the product phase assemblage, but not the reaction rate, to be partly dependent on the carbon source, specificially the particle size and surface area. They also followed the progress of reaction in a carbon/kaolin mixture heated at constant temperature for successively longer times, and they concluded that the 15R phase, likely to accompany the SiAlON, is formed at a late stage by decomposition of β, rather than by nitridation of mullite.

3 Experimental

Three starting mixtures were used in our CTN experiments. In #1 and #2, amorphous silica and fine-grained carbon black 'C1' (Table 1) were mixed with coarse α-Al_2O_3 and fine γ-Al_2O_3, respectively. Kaolin and coarse carbon black 'C2' were used as raw materials in #3. The relative amounts of reactants in the mixtures were calculated according to the stoichiometric composition $Si_3Al_3O_3N_5$. The characteristics of the reactants are given in Table 1. The fine γ-Al_2O_3 was a poorly crystallized decomposition product of ammonium alum. The mineralogical composition of kaolin was mainly kaolinite with about 10% micaceous material, the main impurities being K_2O and Fe_2O_3. The nitrogen gas ('Nitrogen Plus', AGA Co., Lidingö, Sweden), with impurities O_2 (<5 ppm) and H_2O (<5 ppm), was used without further purification. Gas mixtures of 10% CO in N_2 of the same purity were used in some comparison experiments.

Two sample types, pellet and granule, were used with the mixtures #1 and #2, but only granules with #3. Each composition was mixed by grinding an ethanol slurry in an agate mortar for 20 min. The slurry was subsequently dried to a plastic mass, which was extruded to granules (diameter = 1·5 mm and length = 1–6 mm) using a PVC syringe without a needle. Residual alcohol in the granules was subsequently removed by further drying. About 0·4 g powder of the dried slurry was pressed into cylindrical pellets of 11 mm diameter and 8 mm height, using a pressure of 840 MPa for 30 s.

Nitridation was performed in a gas autoclave with a vertical graphite furnace, as described in an earlier publication.[8] The gas-flow rate and the pressure in the autoclave were in the ranges 0·5–10 $l\,min^{-1}$ and 1–50 bar, respectively. Each charge was weighed before and after the reaction and the relative weight change (RWC) calculated as follows:

$$\mathrm{RWC} = \frac{\Delta m}{m_o} \times 100$$

(where m_o is the charge weight)

Approximately 0·4 g of pellets or 0·7 g of granules was charged in a graphite sample holder. Before nitridation the autoclave was flushed three times with 10 bar nitrogen at room temperature and three times during heating. The heating rate was $20°C\,min^{-1}$ and the cooling rate $30°C\,min^{-1}$. The plateau temperature could be held within ±°1C. The gas outlet valve was normally opened at 1350°C on heating and closed at 1300°C on cooling.

The phase composition of the reaction products was analysed by X-ray powder diffraction (XRD, Guinier-Hägg-type focusing cameras) with Cu $K\alpha_1$ radiation and Si as internal standard. The obtained XRD films were evaluated with a computer-linked SCANPI system[16] and the cell parameters of β-SiAlON were calculated by the PIRUM program.[17] The z value of the β-SiAlON phase was the mean of z_a and z_c calculated from the cell parameters by the equations:[18]

$$a = 7{\cdot}603 + 0{\cdot}0296z\ \text{Å} \quad c = 2{\cdot}907 + 0{\cdot}0255z\ \text{Å} \tag{5}$$

The particle morphology of the samples was characterized by scanning electron microscopy (SEM, a Jeol JSM-820 instrument). The impurities in the kaolin raw material and some product powders were measured by EDS, using this microscope equipped with a Link System AN 10000.

4 Results

The relative weight change and resulting phase assemblage of a number of 2 h CTN runs are plotted against annealing temperature in Fig. 2 (starting mixtures #1 and #2) and 3 (mixture #3). The different symbols in the diagrams refer to different sets of synthesis parameters, and the relative size of each sector within a symbol indicates the relative amount of a crystalline phase, as estimated from comparisons of XRD line intensities. This is a

Table 1. Physical and chemical properties of raw materials

Reagent	*Mean particle size*	*BET surface ($m^2 g^{-1}$)*	*Impurities (wt%)*	*Source, grade*
C1	~30 nm	82	H < 6; S, O, N < 1	Nordisk Philblack Co., N330
C2	~70 nm	30	H < 6; S, O, N < 1	Nordisk Philblack Co., N774
α-Al_2O_3	~5 μm	0·55	Alkalies + alkaline earths = 0·1	Fisher Scientific Co., A-591
γ-Al_2O_3	~0·1 μm	38	—	Made in-house
SiO_2	~40 nm	50	$Al_2O_3 < 0{\cdot}08$ $TiO_2 < 0{\cdot}03$	Degussa AB, Aerosil OX50
Kaolin	~5 μm	—	$Fe_2O_3 = 0{\cdot}68$ $K_2O = 1{\cdot}65$ $MgO = 0{\cdot}30$ $Na_2O = 0{\cdot}10$	Partek Höganäs AB, SP-1

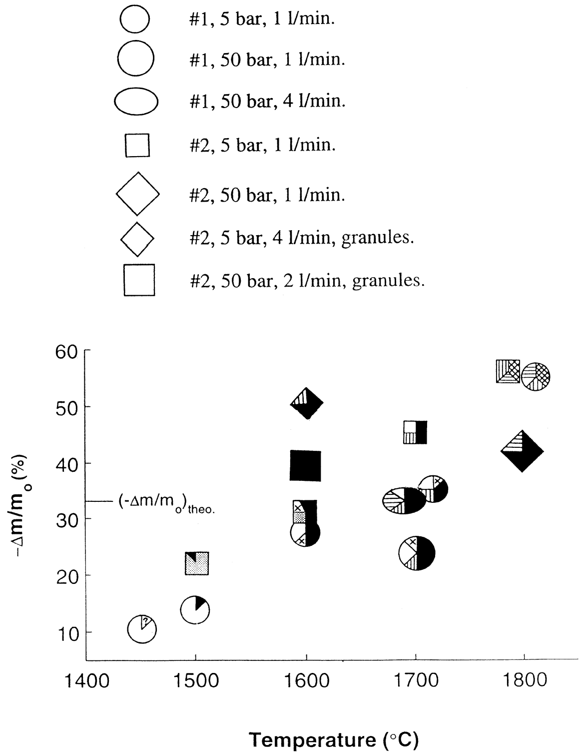


Fig. 2. Conversion ($-\Delta m/m_o$) as a function of temperature for 2 h runs at different $p(N_2)$ and (N_2) with starting mixtures #1 and #2. Resulting phases are indicated by the filling of the symbols as follows: ■ β-SiAlON, □ α-Al_2O_3, ▨ mullite, ▥ 15R ▤ AlN, ▩ SiC. ? unidentified phase and ☒ X phase.

rough measure, semi-quantitative at best, but is nevertheless useful for the following discussion. On some films one or two faint lines were left unidentified, which has been indicated with a question mark in the diagram within the symbol. The theoretical relative weight changes corresponding to full conversion to β-SiAlON, e.g. according to eqn (1), are −33·1 and −40·7% as marked in Figs 2 and 3. A weight decrease in excess of this is indicative of an irreversible loss of SiO(g), or is due to formation of SiC or phases with lower O/N ratios than β-SiAlON.

That SiO(g) evaporation may contribute substantially to the overall weight decrease is evident from Tables 2 and 3, with RWC:s calculated for various product phase assemblages in high-temperature runs with mixtures #1, #2 and #3. The reactions leading to the different products are the following (CO not balanced):

$$3Al_2O_3 + 6SiO_2 + 15C + 5N_2(g) \rightarrow 2Si_3Al_3O_3N_5 + 15CO(g) \tag{6}$$

$$3Al_2O_3 + 6SiO_2 + 21C + 5N_2(g) \rightarrow Si_4Al_6O_2N_{10}(15R) + 2SiC + CO(g) \tag{7}$$

$$3Al_2O_3 + 6SiO_2 + 18C + 4N_2(g) \rightarrow 1/2(Si_4Al_6O_2N_{10}) + 3AlN + SiC + 3SiO(g) + CO(g) \tag{8}$$

$$Al_2Si_2O_5(OH)_4 + 9C + N_2(g) \rightarrow 2SiC + 2AlN + 2H_2O(g) + CO(g) \tag{9}$$

$$Al_2Si_2O_5(OH)_4 + 7C + N_2(g) \rightarrow SiC + 2AlN + SiO(g) + 2H_2O(g) + CO(g) \tag{10}$$

Thus, if only SiC, AlN, CO and H_2O were produced in the run with mixture #3 at 1650°C, 1 bar (Fig. 3), the RWC would amount to ca. 49%. An RWC as high as actually observed, 66%, can only be achieved if a lot of SiO(g) is produced as well (see Table 3).

Figure 2 comprises runs with pellets of mixtures #1 and #2, and some runs performed with a granulated charge. Mixture #3 runs were all made with granules. Figure 3 includes some special runs with mixture #3 in CO/N_2 mixtures and one with the sample contained in an Al_2O_3 crucible with a lid, instead of the open graphite container generally used.

As Fig. 2 shows, β-SiAlON formation in the C + Al_2O_3 + SiO_2 mixtures #1 and #2 barely commenced after 2 h at 1500°C. In the more reactive #2, with fine-grained γ-Al_2O_3, mullite formed, while most of the α-Al_2O_3 starting material in a #1

Table 2. Theoretical relative weight changes calculated for different possible product phase assemblages obtained by various reaction paths with starting mixtures #1 and #2. Also shown is an experimental result from Fig. 2

Reaction	*Eq.* (6)	*Eq.* (7)	*Eq.* (8)	*Experimental result*
Product phases	β-SiAlON	15R + SiC	AlN + 15R + SiC + SiO(g)	AlN + 15R + SiC
$-\Delta m/m_o$(%)	33·1	37·8	54·4	56·2

Table 3. Theoretical relative weight changes calculated for different possible product phase assemblages obtained by various reaction paths with starting mixtures #3. Also shown is an experimental result from Fig. 3

Reaction	*Eq.* (1)	*Eq.* (9)	*Eq.* (10)	*Experimental result*
Product phases	β-SiAlON	SiC + AlN	AlN + SiC + SiO(g)	AlN + SiC
$-\Delta m/m_o$(%)	40·7	49·1	61·6	66·2

pellet was still unreacted after 2 h. On the other hand, 1800°C was too high a synthesis temperature; even with 5 bar overpressure the SiO(g) loss becomes appreciable, and only SiC, 15R and AlN form. The less reactive mixture #1 contains unnitrided α-Al_2O_3 as well. In the useful temperature range between 1500 and 1800°C it can be seen that the product phase assemblage depends on mixture type, pressure, gas flow rate and whether granules (diameter = 1·5 mm, length = 1–6 mm) or pellets (diameter = 11 mm, thickness = 4–5 mm) constitute the charge. Generally, the SiO(g) loss increases with temperature and gas flow rate, (see also Fig. 5), but decreases with increasing pressure. For a particular P, T and Φ set, it is higher for granules than for pellets, and higher for a more reactive mixture. It was finally possible, with mixture #2, to find a suitable combination of process parameters for preparation of a β-SiAlON powder, with $z = 3{\cdot}2$ and free of (crystalline) impurity phases (Fig. 2). This sample was dark greyish, though, and some lines on the XRD film were a little diffuse.

The most reactive mixture, #3, made up of natural kaolin, is equally sensitive to changes in synthesis parameters as #1 and #2 (Fig. 3). Evidently, a high temperature in combination with a low pressure, or a high CO(g) content in the N_2 atmosphere are unfavourable conditions for SiAlON formation. At 1650°C, $p(N_2)$ = 50 bar and a relatively rapid gas flow rate, a β-SiAlON powder free of (crystalline) impurity phases could be prepared after 2 h. The z value of the powder is about 3·2 as calculated from the XRD film.

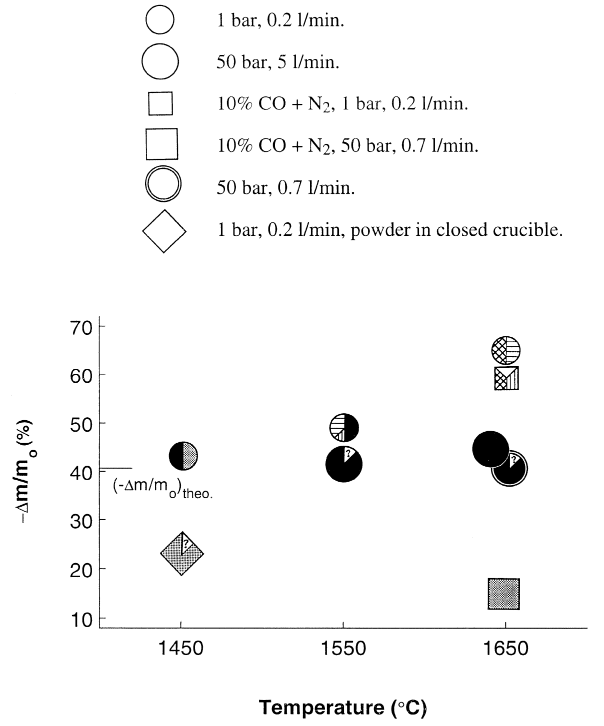


Fig. 3. Conversion ($-\Delta m/m_o$) as a function of temperature for 2 h runs at different $p(N_2)$ and Φ (N_2) with starting mixture #3. Resulting phases are indicated as follows: ■β-SiAlON, □α-Al2O3, ▨ mullite, ▥15R, ▤AlN, [?] unidentified phase and ▩ SiC.

Figure 4 illustrates the progress of reaction in mixtures #1, #2 and #3, as reflected by the phase assemblages obtained after 2, 3 and 5 h heat treatments under a moderate or slow nitrogen flow, $\leqslant 1$ l min^{-1}. The question marks for some #3 samples indicate a certain broadening of some SiAlON peaks or occurrence of narrow multiplets, rather

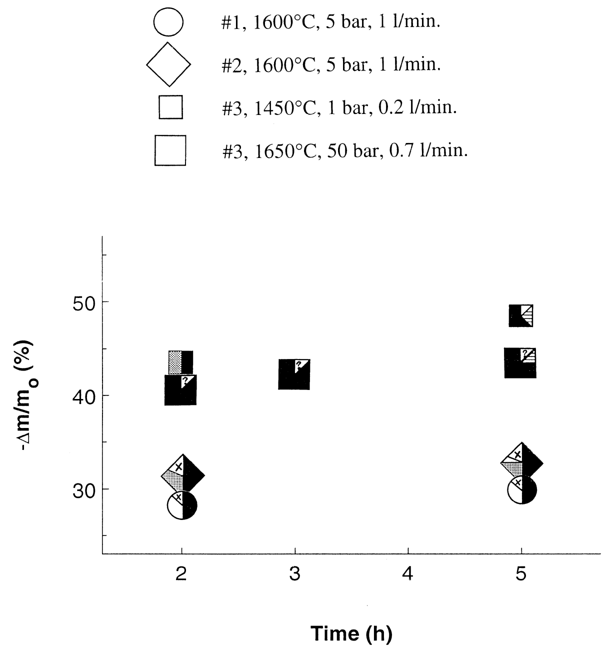


Fig. 4. Conversion ($-\Delta m/m_o$) as a function of annealing time at different $p(N_2)$, $\Phi(N_2)$ and temperatures with different mixtures. ■β-SiAlON, □α-Al_2O_3, ▨mullite, ▤AlN, [?]unidentified phase and ☒X phase.

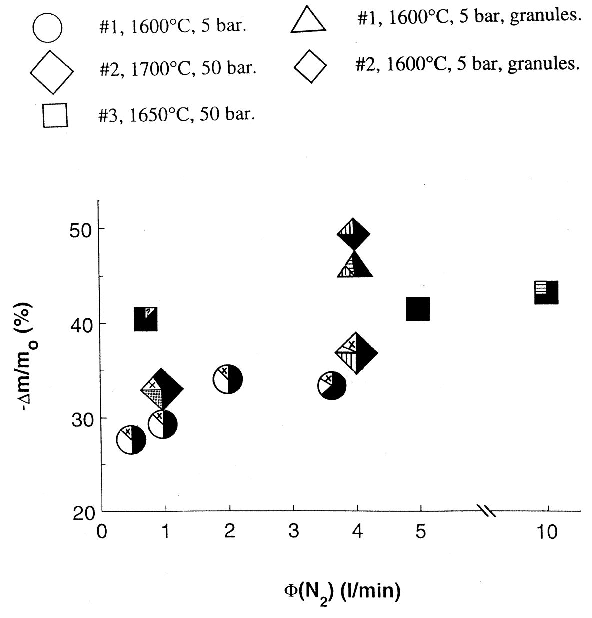
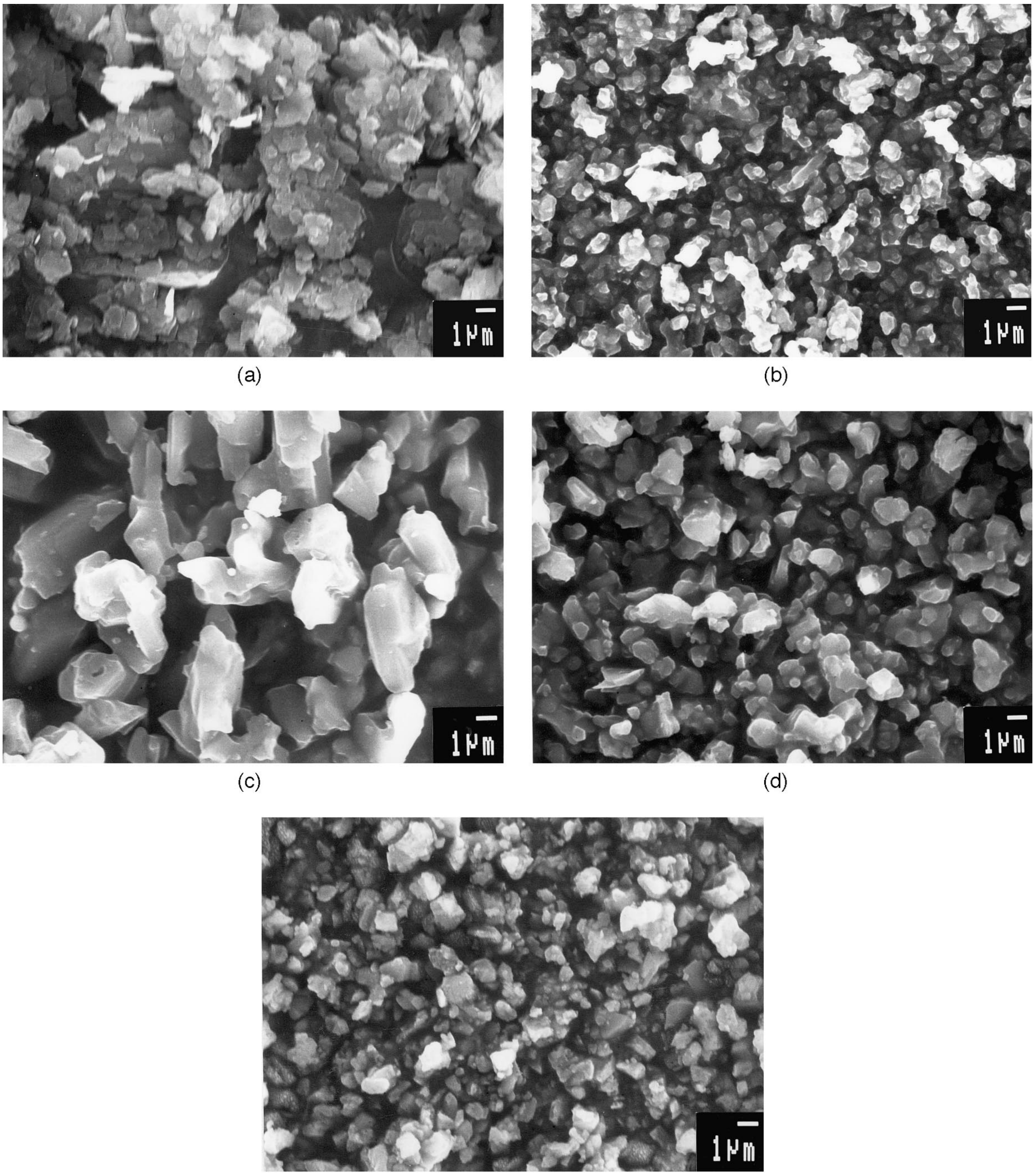


Fig. 5. Conversion ($-\Delta m/m_o$) as a function of gas-flow rate for 2 h runs at different temperatures and pressures with different mixtures. ■β-SiAlON, □α-Al_2O_3,▨ mullite, ▥15R, ▤AlN, [?] unidentified phase and ☒X phase.

than distinctly different sets of reflections attributed to impurity phases.

Figure 5 highlights the effect of gas flow rate on the synthesis result at T = 1600–1700°C. Clearly, the nitridation rate increases with increase of flow rate, due to an improved venting of CO(g) from the sample space.

In the present study, products with widely variable particle size and morphology were obtained depending on the pressure, gas-flow rate, charge type and raw material type. As shown in Fig. 6(b)–(e), the powders prepared from kaolin (#3) generally had a narrow particle size distribution, compared to Al_2O_3/SiO_2 mixtures (Fig. 8) and were comprised of discrete particles, different from the kaolin starting material [Fig. 6(a)]. At 1650°C and 50 bar, the β-SiAlON particle size varied from $\sim$0·8 to 5 m, depending on the N_2 gas-flow rate [Fig. 6(c) and (e)]; the most fine-grained powder was obtained with the highest flow ($10\ \mathrm{l\,min^{-1}}$). The particle size also increased slightly with temperature [Fig. 6(b)–(d)]. The particle size of the raw materials was apparently not an important parameter. As a matter of fact, β-SiAlON formed from the intermediate mullite phase



(a) (b) (c) (d) (e)

Fig. 6. SEM photos of the kaolin raw material and the #3 samples, run at 50 bar, at different temperatures and gas-flow rates for 2 h: (a) the kaolin raw material; (b) pure β-SiAlON product, run at 1550°C, $5\ \mathrm{l\,min^{-1}}$; (c) pure β-SiAlON product, run at 1650°C, $0{\cdot}7\ \mathrm{l\,min^{-1}}$; (d) pure β-SiAlON product, run at 1650°C, $5\ \mathrm{l\,min^{-1}}$; (e) pure β-SiAlON product, run at 1650°C, $10\ \mathrm{l\,min^{-1}}$.

[Fig. 7(b)–(c)], which was much coarser than the raw materials [Fig. 6(a)]. Two special runs were performed with mixture #3 in a 10% CO/N_2 gas mixture [Fig. 7(a)–(b)]. At high pressure (50 bar) and 10% CO, both nitridation and SiC formation ceased. The morphology of the mullite produced [Fig. 7(b)] was similar to that of the kaolin decomposition product in pure nitrogen [Fig. 7(c)]. At 1 bar and 10% CO, the product was a mixture of SiC, 15R and Al_2O_3 with an irregular grain shape and a wide size distribution [Fig. 7(a)], reflecting the complex scheme of parallel reactions involved. There are also some morphological differences between samples prepared from pellets and granules of mixtures #1 and #2 (Fig. 8). Pellet samples produced powders with irregularly shaped grains and a wide size distribution, while granules usually gave relatively discrete and uniform particles.

In most runs, Si_3N_4 whiskers often formed on the granule surfaces and the supporting graphite

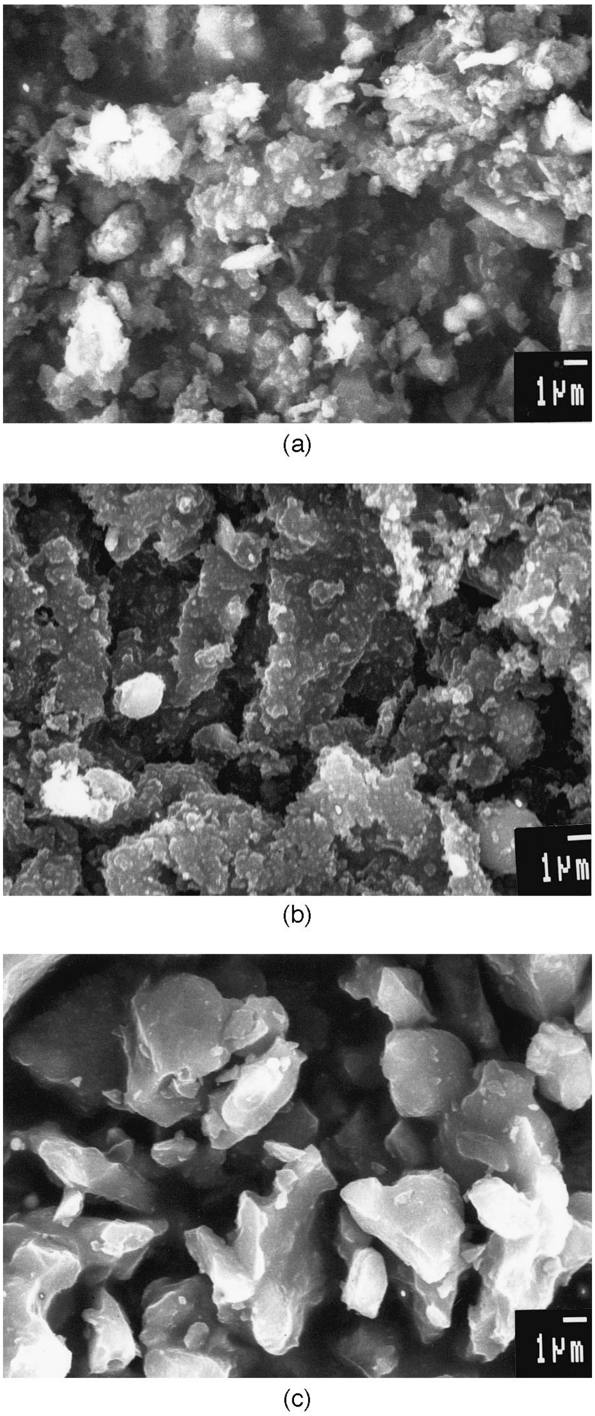


Fig. 7. SEM photos of the #3 samples, run at 1650°C for 2 h in 10% CO + N_2 gas mixtures, and of the mullite intermediate phase prepared in N_2: (a) #3, run at 1 bar and 0·2 l min^{-1}; (b) #3, run at 50 bar and 0·7 l min^{-1}. (mullite); (c) The kaolin run at 1420°C for 1 h in N_2 atmosphere (mullite).

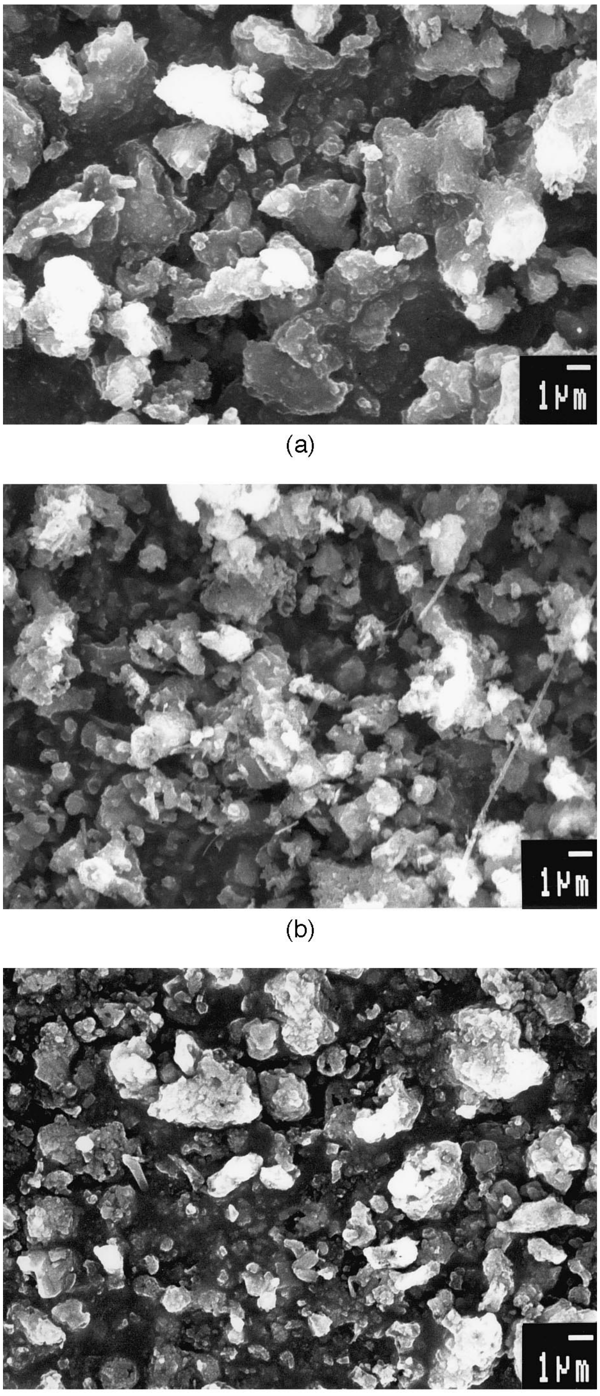


Fig. 8. SEM photos of the samples run at 1600°C for 2 h, 5 bar and 4 l min^{-1}: (a) #1, charged as a pellet; (b) #1, charged as granules; (c) #2, charged as granules.

foil, especially at temperatures above 1600°C and pressures below 5 bar. High pressures hampered the whisker formation.

Microarea elemental analyses of the kaolin raw material by EDS showed that the K, Fe, Mg and Na impurities were uniformly distributed in the samples, and that the impurity levels were approximately those specified by the supplier. Traces of Ca and S were concentrated in a few particles. After running at ~1500°C for 2 h, the Fe and Mg contents of a mixture #3 were unchanged, but K and Na could not be detected.

5 Discussion

The results of the present study confirm, on the whole, the reaction sequence suggested by previous authors: initial decomposition of kaolin to mullite (+ amorphous silica, probably), followed by nitridation to β-SiAlON and, on continued heating, also to 15R and AlN. The Al_2O_3/SiO_2 mixtures react to mullite but, as expected due to the poor reactivity relative to mixture #2, mixture #1 mainly comprises unreacted α-Al_2O_3 even after 2 h at 1500°C (Fig. 2), while #2 is fully converted to mullite. However, the alumina found in some samples is evidently formed secondarily, for instance in the 5 h run with mixture #2 (Fig. 4). This may be due to decomposition of mullite under the reducing conditions in a graphite furnace, as suggested by previous workers.[10] The X-phase is transient, as expected from the phase diagram, but Fig. 4 indicates an almost steady state in mixtures #1 and #2 over long reaction times at 1600°C between the phases in the sequence:

$$Al_2O_3 + SiO_2 \rightarrow \text{mullite} \rightarrow \text{X-phase} \rightarrow \beta\text{-SiAlON}$$

In mixture #1 the first step is relatively slow.

A pressure increase reduces the SiO loss, resulting in a smaller relative weight change and improved compositional control. This is supported by the observation that hardly any Si_3N_4 whiskers were observed in high pressure runs. SiC formation at high temperatures was suppressed in favour of nitride phases at 50 bar. This is consistent with the pressure-induced Si_3N_4/SiC transformation previously observed, and is also predicted by thermodynamic calculations on the Si–O–N–C system.[7] At 50 bar, β-SiAlON synthesis was accomplished even at 1800°C with no trace of SiC (Fig. 2).

Whether a pellet or a granule charge was used made a large difference as to conversion, at least for moderately high N_2 pressures. It can be seen in Fig. 5 that no residual α-alumina is found in granules of mixtures #1 and #2 at 1600°C, 5 bar, 4 $l\,min^{-1}$, and that the relative weight change is appreciably higher than with pellets. The critical pellet diameter reported by Kokmeijer *et al.*, below which the conversion is size-independent, was about 2 mm at 1450°C.[15] The difference in conversion rate encountered in our experiments seems to verify the existence of such a critical size, being around 5 mm at 1600°C, which was the pellet diameter and thickness. Alternatively, the difference may be due to the larger specific surface area of a granulated charge, and thus a larger reducing action exerted by the gaseous environment, compared with pellets.

Figure 5 shows that nitridation proceeds faster in a #2 pellet at 4 $l\,min^{-1}$ than at 1 $l\,min^{-1}$, even at 1700°C. This is mainly an effect of more efficient CO(g) removal by a rapid flow, which was demonstrated by Higgins and Hendry,[4] but part of the extra weight decrease at 4 $l\,min^{-1}$ may be ascribed to enhanced SiO(g) loss. With granules of the more reactive mixture #3, the flow rate dependence in 2 h runs was not as marked. At a rate of 5 $l\,min^{-1}$ the reduction/nitridation has evidently not reached the upper limit, as in a #3 granule under a flow of 10 $l\,min^{-1}$ AlN appears together with β-SiAlON.

As expected, β-SiAlON formation is retarded by increased p(CO). By thermodynamic calculations Higgins and Hendry predicted mullite to be the only stable phase above 20% CO at 1450°C and atmospheric pressure of nitrogen.[4] SiC was the main phase and 15R the only nitride phase in our #3 sample run for 2 h at 1650°C, 1 bar in 10% CO/N_2 (Fig. 3). A 50 bar run in such a gas mixture produced pure mullite, SiC formation was not observed. A #3 mixture, run at 1450°C in a sample holder with a lid, turned out to be poorly reacted after 2 h, leaving mainly mullite as product phase. The similarity of results between the special runs in Fig. 3 suggests that CO removal, and thus sample holder design, is a critical parameter. It also supports the idea[15] that the reaction rate dependence on granule size is due to pore diffusion control of CO, and that this is rate-determining at low temperatures and/or large pore sizes.

AlN appears in the samples on prolonged annealing or at high gas flow, which has been observed previously.[3] The source may be Al_2O_3 stemming from decomposed mullite, as suggested by Cho and Charles,[10] or a reductive decomposition product of β-SiAlON.

A key problem in SiAlON powder synthesis by CTN, encountered in previous work and also evident from our data, thus seems to be to suppress competing reactions. Particularly in starting mixtures that are poorly reactive and require extended annealing, compositional shifts due to SiO(g) evaporation my be substantial. Increasing the pressure was a means to reduce the SiO loss, even in a rapid gas flow, and also to speed up β formation by increase of temperature without having SiC formed concurrently. A high gas flow rate must be used in order to remove CO efficiently from the sample space, but at the same time it makes parts of the sample amenable to overreduction, particularly if a graphite furnace is used. As shown by the #2 runs at 1600°C in Fig. 2, pressure and gas flow can be balanced to produce a monophasic SiAlON powder.

A high gas-flow rate, $5\ \mathrm{l\,min^{-1}}$, seems to favour formation of a fine grained β-SiAlON product from kaolin and carbon mixtures [Fig. 6(b) and (d)]. It is quite interesting that the particle size could be controlled by the nitrogen gas-flow rate [Fig. 6(c)–(e)] in about the same way as previously found in high–pressure carbothermal preparation of AlN.[19] In that work[19] a tendency was noted towards smaller AlN particle size with increasing pressure and gas flow rate, which was interpreted as being due to these parameters influencing gas phase reaction steps in the AlN formation process.

In carbothermal synthesis of Si_3N_4 from SiO_2, the evidence for gas phase formation reactions is even stronger, as several investigators report substantial Si_3N_4 whisker growth on granulated charges.[20–22] The gaseous precursor is SiO(g), which may build up partial pressures of the order of 10^{-2} bar in a C/SiO_2 mixture at about 1500°C, according to thermodynamic calculations.[22] Further support that may be quoted for suggested precipitation reactions from the gas phase, in the case of Si_3N_4[23] and AlN,[19] is the homogeneous particle size and shape observed. Detailed mechanisms for these precipitation reactions, however, still remain to be elucidated.

It is tempting to predict that gas phase reaction steps are involved also in SiAlON particle formation. The particle size dependence on gas flow rate, at least for a C/kaolin mixture, is one reason; another is the observed large difference in particle size between the kaolin raw material, the intermediate mullite phase and the product powder. As seen in Figs 6 and 7, the coarse kaolin starting material with a wide particle size distribution has transformed into a fine, relatively homogeneous SiAlON powder. One obvious difference between SiAlON powder on the one hand and AlN and Si_3N_4 powders on the other is the irregular grain shape in the former case, indicating a more complex formation reaction than just precipitation from an SiO(g)- and Al(g)- supersaturated nitrogen gas. The observed decrease in particle size with increase in gas flow rate for SiAlON may be interpreted, as previously in the case of AlN,[19] as a consequence of the seed formation being enhanced by more efficient removal of CO(g) from the sample space with a higher gas flow. This should also explain why pellet samples of #1 show low conversion and wide grain size distribution, compared with granules [cf. Figure 8(a) and (b)]. A special run, identical with the one leading to the sample in Fig. 6(e), except for a rapid gas flow ($10\ \mathrm{l\,min^{-1}}$.) being maintained only during heating-up and then reduced to $0{\cdot}7\ \mathrm{l/min^{-1}}$ for the remaining 2 h, produced a powder equally fine-grained. This shows that the final SiAlON particle size is determined during the initial synthesis period (nucleation), and that the gas flow rate (p_{CO}, p_{O2}) does not control the grain growth to any large extent.

That the number of β-SiAlON seeds is partly controlled by CO(g) concentration (i.e. oxygen partial pressure) suggests that the final reaction step is reductive, for instance of the type:

$$\text{X-phase} \rightarrow \beta\text{-SiAlON} + O_2(g)$$

supported by:

$$2C + O_2(g) \rightarrow 2CO(g)$$

However, silicon and nitrogen must be added simultaneously for adjustment of stoichiometry, and SiO(g) is the candidate Si-bearing species. We are not able, on the basis of our present data, to deduce this last step in the reaction sequence from kaolinite or Al_2O_3/SiO_2 to β-SiAlON. Possibly, SiAlON seeds are formed by the action of SiO(g) on reduced spots on solid particles, making these crumble into small irregular pieces, as seen on the micrographs.

Thus, the main advantage of using an elevated nitrogen pressure in carbothermal preparation of SiAlON, as well as of Si_3N_4, seems to be an improved compositional control of the charge by avoiding SiO loss. In both cases SiC formation is also suppressed at elevated $p(N_2)$, for thermodynamic reasons, even at high reaction temperatures. No positive influence on the nitridation kinetics by an increased $p(N_2)$, such as that observed in AlN synthesis, was found in case of SiAlON and Si_3N_4, however.

The SiAlON formation rate was found to be faster with kaolin as starting material than with Al_2O_3/SiO_2. This is a known fact, which has been ascribed to the intimate mixing of the reactants in kaolin, but also to the promoting action of various impurities in the natural material.[24] Some impurities, such as iron, may form transient silicide or silicate liquids, with an ability to dissolve nonvolatile constituents and improve transport of reactants.

Al_2O_3/SiO_2 mixtures apparently form mullite as a first step in the carbothermal nitridation process (Figs 2 and 4), which makes us think that the reaction sequence from this point to SiAlON should be the same as in runs with kaolin as starting material. One difference between the two routes, though, apart from the overall reaction rate, is evident from our XRD results and may be noted. With kaolin, no line belonging to the X-phase is detectable on the Guinier films, while this compound clearly is an important intermediate phase in the Al_2O_3/SiO_2 runs (Figs 2 and 4). The reason could be that SiAlON formation in fact occurs by different schemes, depending on the starting material. With Al_2O_3/SiO_2, there may be a sequence of solid-gas reactions, including X-phase. With kaolin, transient liquid is expected to form and therefore some liquid-solid-gas mechanism may be operating.

As shown by SEM and EDS analyses, alkali metal impurities such as K and Na in the kaolin raw material are almost completely removed during the high temperature runs, probably by irreversible evaporation and/or intercalation in the graphite crucible material. They are therefore less influential impurities. Mg and Ca in the products could not be found by XRD but may be present in a glass phase, as EDS showed that their amounts did not change during the reaction.

A further study of the carbothermal synthesis of β-SiAlON powders is now in progress at this laboratory, including the effect of other parameters on morphology and thermodynamic calculations of pertinent equilibrium compositions in the Si–Al–C–O–N system at different temperatures and pressures.

6 Conclusions

1. Monophasic β-SiAlON powders ($Si_{6-z}Al_zO_zN_{8-z}$ with $z \sim 3$) can be produced by carbothermal nitridation of kaolin or Al_2O_3/SiO_2 mixtures at ~1600°C for 2 h, under a pressure of 50 bar and a gas-flow rate$\geqslant 21\ \mathrm{l\,min^{-1}}$. Syntheses with the same precursors but at lower pressure did not produce monophasic β-SiAlON powders.
2. The use of an elevated nitrogen pressure is advantageous, as evaporative losses of SiO(g) are reduced, and a higher synthesis temperature is permitted than at atmospheric pressure, without leading to SiC formation.
3. The SiAlON particle morphology can be controlled to some extent by a proper choice of raw materials, gas flow rate and pressure, so that a minimum particle size (~1 μm) is obtained at a high flow.

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