JOURNAL OF MATERIALS SCIENCE 30 (1995) 6363–6369

Carbothermal production of β′-sialon from alumina, silica and carbon mixture

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Mixtures of pure nanometer-sized amorphous silica and γ-alumina with the atomic ratio Si:Al = 1 were reduced by a stoichiometric amount of carbon between 1100 and 1450 °C in flowing nitrogen in order to produce β′-sialon powder. Using aqueous suspensions of starting materials, compacts with different microstructures were prepared for reaction. Silica reduction to SiO occurred at a temperature as low as 1300 °C and part of it was removed with flowing nitrogen. Carbothermal reaction involving nitrogen stated at 1350 °C and Si_2N_2O was found as an intermediate together with SiC, resulting in β′-sialon formation. Loss of silica from the system led to AlN formation. Decomposition of β′-sialon into sialon polytypoids (15R, 12H) was observed as a result of sialon and AlN reaction at 1450 °C. The reaction rate of sialon formation was slowed down compared to the carbothermal reduction of kaolin because of the lack of impurities. The microstructure of the reacted pellets influenced the reaction products, and the narrow pore size distribution as well as good homogeneity enhanced β′-sialon formation.

1. Introduction

Sialon ceramics appear to be very attractive engineering materials which can replace silicon nitride ceramics in some applications. The sialons can be produced by reaction sintering of a mixture of Si_3N_4, AlN and Al_2O_3 [1], as well as by carbothermal reduction of the appropriate oxides. The last reaction offers the advantage of low cost starting materials. Lee and Cutler [2] were the first to describe the reaction of a clay–carbon mixture with nitrogen. Although the overall reaction equation

$$3(2SiO_2Al_2O_32H_2O) + 15C + 5N_2 \rightarrow 2Si_3Al_3O_3N_5 + 15CO + 6H_2O \quad (1)$$

appears very simple, the extensive studies on this subject showed that the reaction rate and product are sensitive to a number of factors: gas flow rate [3, 4], the Reynolds number [5, 6], the size of the reacting pellets [7], contamination by impurities in raw materials [3, 5, 7] and other parameters of the reaction [8].

One of the most important factors influencing this reaction is the source of raw materials. The aluminosilicate minerals like different types of kaolin [2–5, 7], New Zealand halloysite [9], montmorillonite [10], fire clay [11, 12], mixtures of fused silica, boehmite and bayerite [13] provide different amounts of impurities and primary microstructure resulting in a variety of reaction sequences as well as sialon accompanying products.

The aim of the present study is to compare the sequence of reactions performed from very pure starting materials with that from aluminosilicate minerals. Slip casted tablets from the suspensions of nanometre sized, pure alumina, silica and carbon formed the basis for this work. Nanometre sized particles of both alumina, silica and carbon having a Brunauer–Emmett–Teller (BET) surface area of about 27 $m^2 g^{-1}$ gave the possibility of obtaining a sufficiently homogeneous distribution of the three components. Moreover, this procedure has the advantage that it enables the microstructure to be changed by changing the stability of the constant chemical composition suspension. The influence of time and temperature as well as the microstructure on the reaction product has been examined using quantitative X-ray diffraction (XRD) analysis.

2. Experimental procedure

Amorphous fumed silica (Aerosil OX50, Degussa), γ-alumina (Alumina C, Degussa) and carbon (Elftex 125, Cabot) were used as starting materials.

The starting powders were weighed out according to Equation 1, mixed with water surfactant and adjusted to the desired pH. CG-6 was chosen as a suitable surfactant to obtain sufficient distribution of coal in water. Nitric acid and NH_4OH were used for pH adjustment and after the sedimentation test [14] suspensions with pH < 2 were found to be the most stable. Flocculation and gel formation occurred at pH

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5–8. Triton X-100, known as a good surfactant for water suspensions of coal [15], caused strong gel formation of alumina–silica water suspensions and because of this it has been chosen for gel preparation with supposed good coal distribution.

The mixtures of the relevant ingredients, after being mixed on a roller bench and ultrasonically treated (10 min) in order to break agglomerates were then slip casted onto a plaster of Paris support into a plastic ring (in the case of the suspension) or allowed to dry (in the case of the gel). The specimens were labelled as follows:

1. G-1 tablets from the flocculated suspension prepared from a mixture of 350 g of water, 0.74 g of CG-6 surfactant, 10.64 g of carbon, 21.27 g of Aerosil, 18.08 g of Alumina C. NH_4OH was added up to gel formation with $pH = 5.5$.
2. T-2 tablets from stable suspensions with CG-6 as a surfactant and $pH < 2$.
3. G-3 gel formed as a result of Triton X-100 surfactant addition without any pH adjustment.

All specimens were dried at 40 °C and then kept at 105 °C before use in the reaction. The specimens were placed in a horizontal tube furnace, heated at a rate of $5\ K\,min^{-1}$ in a nitrogen flow of $12\,l\,h^{-1}$ and soaked at a chosen temperature between 1100 and 1450 °C. The following nitridation runs were performed

1. Reaction 1: A low mass experiment with T-2 slip casted tablets (tablets with a diameter of 28 mm and 4–6 mm height, weighing 2.5–3.0 g) for
   (a) 2 h soaking at 1100–1450 °C,
   (b) soaking at 1450 °C for 30 min–6 h, and
   (c) soaking at 1300 °C with nitrogen flow of $0–12\,l\,h^{-1}$.
2. Reaction 2: medium mass experiment, 20 g of starting tablets or gel, 14–16 h soaking at 1450 °C with $12\,l\,h^{-1}$ nitrogen flow.
3. Reaction 3: large mass experiment, 300 g of tablets and gel at about 1470 °C for 19 h with nitrogen flow of $35\,l\,h^{-1}$.

The reactions with medium and large mass were followed by monitoring the concentration of carbon monoxide in the exhaust gas (Defor gas analyser, Maihak). Reactions 2 and 3 were terminated when no more CO developed, respectively, after 14 and 19 h. The other parameters of the large mass experiment ($35\,l\,h^{-1}$ N_2 flow at 1470 °C) were the same as for carbothermal production of β′-sialon from kaolin in a 500 g run [7]. The specimens were weighed before and after nitridation, and then examined in a thermobalance (Netzsch STA 409).

The composition of the products was determined by (XRD) with CuK_α radiation and 2Θ ranging from 10 to 70° using a Rigaku microdiffraction system. A quantitative analysis was performed from the measured intensities. Two possible methods were compared [16, 17]: the first is based on the adiabatic principle of autoflushing and the second applies corundum as a reference material.

Of these two the first one easily leads to wrong conclusions when amorphous phases are present. Since this is often the case for silicon based ceramics, the second method has been used in this study. Using mixtures with known amounts of relevant components, one comes to the conclusion that the accuracy of this method is better than 5% if the diffraction lines are well resolved.

Sample characterization was performed with the aid of a mercury porosimeter (Pore Sizer 9310, Micromeritics) as well as by scanning electron microscopy (SEM) observation of the surface of the reacted specimens. The condensation product which formed on the surface of the specimens and at the end of the tube furnace was examined using SEM and transmission electron microscopy (TEM).

3. Results

3.1. Carbothermal reaction of slip casted tablets

A study of the influence of temperature on carbothermal reaction has been performed on T-2 tablets. A single tablet was heated at a rate of $5\ K\,min^{-1}$ in a nitrogen flow of $12\,l\,h^{-1}$ and soaked for 2 h at a chosen temperature between 1100 and 1450 °C. Changes of the microstructure after reaction at a given temperature are presented in Fig. 1. Phase composition from the X-ray analysis is given in Fig. 2. The second column of Table I shows the mass loss during carbothermal reaction. When the reaction product was investigated in a thermobalance first, weight loss occurred, from which the residual carbon content was calculated. At higher temperatures, after carbon was completely removed, some mass gain was observed (column 4 in Table 1).

The increase of carbon content after reaction at 1100 and 1200 °C is due to the carbonization of CG-6 surfactant.

The first traces of the reaction are visible after heating at 1300 °C. Mullite crystallization is connected with a significant drop in surface area (Fig. 1). Unexpected mass losses during the reaction and traces of the reduction product in these specimens indicate the loss of silica from the sample

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)} \qquad (2)$$

where s and g stand for solid and gas, respectively.

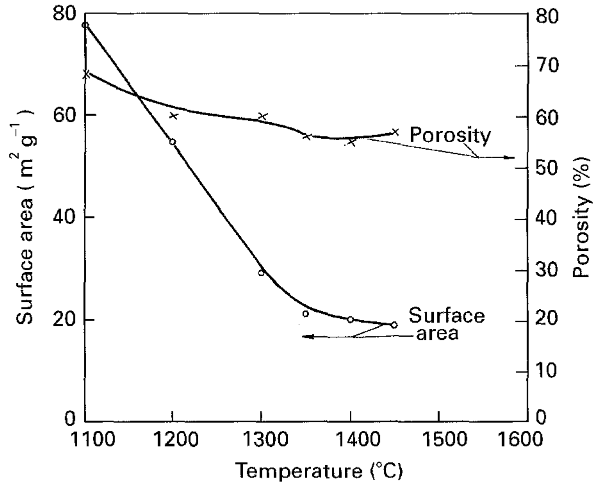

Figure 1 Changes in microstructural parameters as a function of reaction temperature.

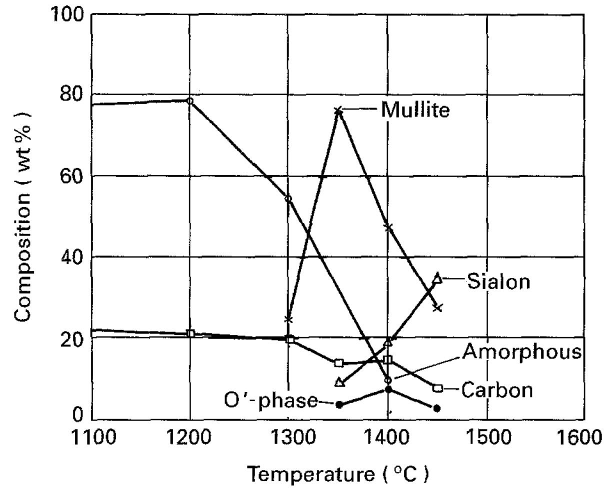

Figure 2 Phase composition in wt % reaction product after 2 h at the reaction temperature.

TABLE I Mass losses during reaction, residual carbon and phase composition versus reaction temperature in nitrogen flow $(\mathrm{l\,h^{-1}})$

Reaction temperature (°C)	Mass loss[a] (wt %)	Residual carbon[b]	Mass gained[c]	Phase composition
Starting tablets	–	21.2	–	Amorphous silica γ-alumina Carbon
1100	4.7	22.3	–	Amorphous γ-alumina Carbon
1200	6.1	21.4	–	Amorphous γ-alumina Carbon
1300	14.4	19.8	1.6	Mullite, amorphous α-cristobalite δ-alumina, carbon
1350	22.0	13.8	4.6	Mullite, O' β-sialon Carbon
1400	27.0	15.2	6.2	Mullite, β-sialon O' Carbon
1450	28.0	8.2	8.0	β-sialon, mullite AlN, O' Carbon
Theoretical	31.9	–	–	β-sialon

[a] Mass loss during reaction.

[b] Residual C content in wt % after reaction, determined from TGA.

[c] Mass gain in wt % after carbon removal, determined from TGA.

From Table I, one finds that 21.4–19.8 = 1.6% carbon is lost going from 1200 to 1300 °C; if this is completely converted according to Equation 2, a mass loss of 8.8% should occur. This is in good agreement with the observed mass loss of 14.4–6.1 = 8.3%.

The rate of Equation 2 depends on the partial pressure of the reaction products which are diluted in the flowing nitrogen. Decrease of nitrogen flow can cause increase of the partial pressure of the reaction products and slow down the rate of Equation 2. In order to confirm that mass losses at lower temperatures before the nitrogen involving reaction started, were due to silica reduction, the following experiment has been performed. Tablets T-2 were heated at 500 °C for 15 min in order to remove surfactant and nitric acid and then kept at 105 °C. Each tablet was then inserted into the horizontal tube furnace and reacted for 2 h at 1300 °C with 2.5, 5.0 and 12.0 $\mathrm{l\,h^{-1}}$ nitrogen flow. Moreover, one of the tablets reacted without nitrogen flow, which was switched off at 1200 °C during heating and then allowed to flow during cooling below 1200 °C in order to prevent oxidation. Mass losses during the reaction and the residual carbon content from thermogravimetric analysis (TGA) are shown in Table II. The mass loss clearly increases with increasing nitrogen flowrate. Data in column 4 of this table indicate the presence of some oxidizable compound in the reaction product after carbon has been removed. In the XRD pattern of the sample reacted in an N_2 flow of 12 $\mathrm{l\,h^{-1}}$ at 1300 °C, traces of O' phase (Si_2N_2O) were observed. This may account for the mass gain during oxidation.

TABLE II Mass losses after reaction, with different nitrogen flow at 1300 °C and mass changes of the reaction product from TGA measurement in air

Nitrogen flow flow $(\mathrm{l\,h^{-1}})$	Mass loss (wt %)	Residual carbon (wt %)	Mass gained during oxidation (wt %)
Static N_2	2	18.5	–
2.5	6	19.3	0.4
5.0	10	17.8	1.2
12.0	13	16.6	1.7

High nitrogen flow caused formation of a spider web-like cover on the surface of the specimen. TEM–Energy dispersive spectroscopy (EDX) analysis of this product (Fig. 3) showed that it consisted mainly of a silica reduction product, however, it was not possible to determine what form it was. Fur-like deposits on the surface of the pellet reacted at 1450 °C in high nitrogen flow were reported by Cho and Charles [18]. By XRD analysis these deposits were confirmed to be α-Si_3N_4 whiskers.

Reaction with nitrogen starts at 1350 °C. It leads to significant mass losses and a further drop in the surface

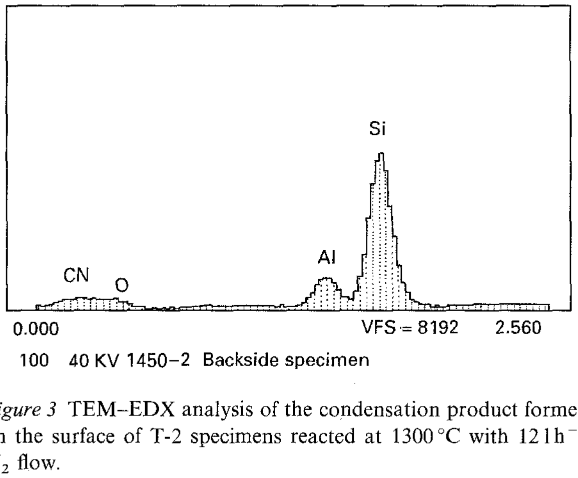

Figure 3 TEM–EDX analysis of the condensation product formed on the surface of T-2 specimens reacted at 1300 °C with 12 $\mathrm{l\,h^{-1}}$ N_2 flow.

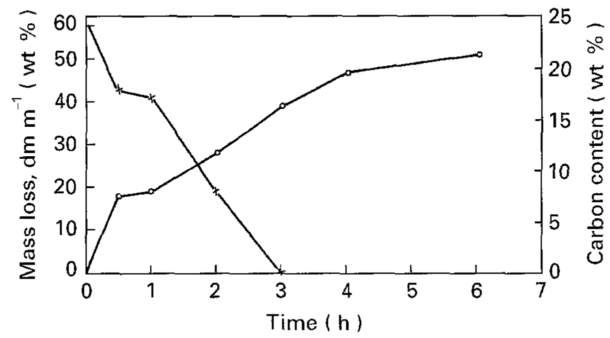

Figure 4 Mass losses (O) and carbon content (×) as a function of reaction time at 1450 °C with 12 l h^{-1} N_2 flow.

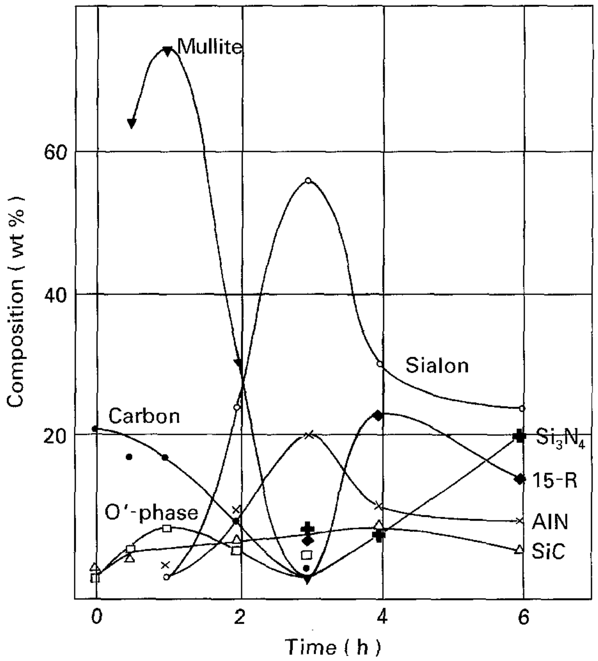

Figure 5 Phase composition of the reaction product versus reaction time at 1450 °C.

area and porosity. Besides mullite crystallization the formation of O′-phase and β′-sialon was observed. Only traces of SiC were observed as accompanying products of β′-sialon formation.

A higher reaction temperature leads to a greater amount of β′-sialon together with mullite decomposition.

The influence of time on carbothermal reduction at 1450 °C has been investigated on T-2 tablets in a low mass experiment. The mass losses and carbon content after reaction are presented in Fig. 4. Phase composition is shown in Fig. 5.

It has been found that all the carbon was consumed after 3 h reaction. Mass losses were higher (39 wt %) than can be calculated from Equation 3., i.e. 31.9 wt %

$$6SiO_2 + 3Al_2O_3 + 15C + 5N_2 \rightarrow 2Si_3Al_3O_3N_5 + 15CO \qquad (3)$$

Moreover, they increased with prolonged reaction time, although there was no more carbon in the system.

At the beginning of the reaction at 1450 °C O′-phase (Si_2N_2O) formed and then disappeared at the same time as mullite and carbon.

Identification of β-SiC in the presence of β′-$Si_3Al_3O_3N_5$ by XRD is rather difficult, because its strongest diffraction line of $d = 0.252$ nm (29–1129 JCPDS) is overlapped by a β′-sialon line of $d =$ 0.252 nm with a relative intensity of $I/I_0 = 93\%$ (36–1333 JCPDS). Accuracy of calculation of β-SiC amount is rather low, as it can be calculated from the intensity of the weak $d = 0.15411$ nm line. Comparing the intensities of both lines there are indications that silicon carbide is present in the reaction product at a constant level independent of the time of reaction.

Continued reaction resulted in β′-sialon formation together with AlN. The maximum values of β′-sialon content, as well as the disappearance of carbon in the specimens, were found after 3 h reaction. Soaking of the specimens at 1450 °C for longer than 3 h leads to decomposition of β′-sialon and AlN, together with increasing amounts of 15-R and 12-H phases.

3.2. Influence of pellet microstructure on β′-sialon formation

The influence of pellet microstructure on β′-sialon formation has been studied in medium and large mass experiments. The results of the porosimetry study are given in Table III. The main difference between specimens from the gel-like and stable suspensions is the significant amount of larger pores in the former. All of the suspensions have the same surface area because of the nanometre sized particles of the starting powders. A different method suspension preparation resulted in narrow pore size distribution in the tablets from stable suspensions. However, the overall porosity of the gel derived specimens is higher and the average diameter of the pores is larger. The second difference could be due to poorer coal distribution in gel derived specimens, as they are not entirely black.

Phase compositions of the specimens reacted in medium and large mass experiments are given in Table IV. XRD patterns of T-2 tablets and G-3 gel

TABLE III The microstructure of as-prepared slip casted and gel specimens

	G-1	T-2	G-3
Surface area, m^2 g^{-1}	77.6	77.2	78.1
Average pore diameter, μm	0.05	0.037	0.099
Apparent density, g cm^{-3}	0.68	0.86	0.59
Porosity, %	68.8	61.4	72.0

TABLE IV Phase composition of the specimens from 20 g run with different microstructure reacted at 1450 °C

Phase (%)	G-3 gel (14 h)	T-2 tablets (14 h)
β′-sialon	68	81
15-R	6	–
AlN	18	14
SiC	4	5
Al_2O_3	4	–

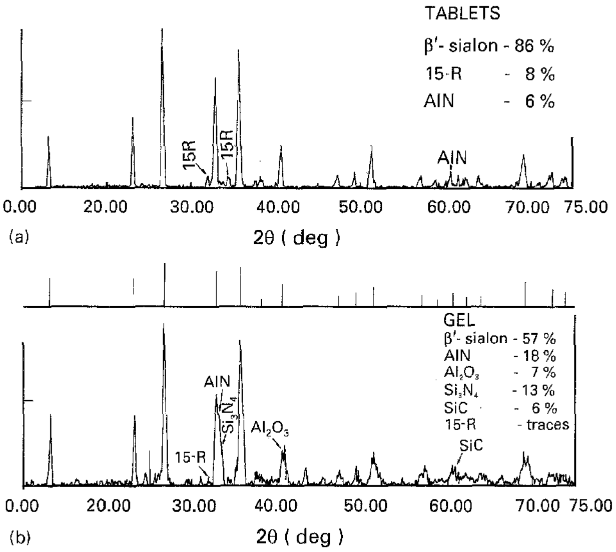

Figure 6 XRD pattern of (a) T-2 tablets and (b) G-3 gel reacted at 1470 °C with 35 l h^{-1} N_2 flow in the large mass experiment. For (a): β′-sialon = 86%, 15-R = 8%, AlN = 6%. For (b): β′-sialon = 57%, AlN = 18%, Al_2O_3 = 7%, Si_3N_4 = 13%, SiC = 6%, 15-R = traces.

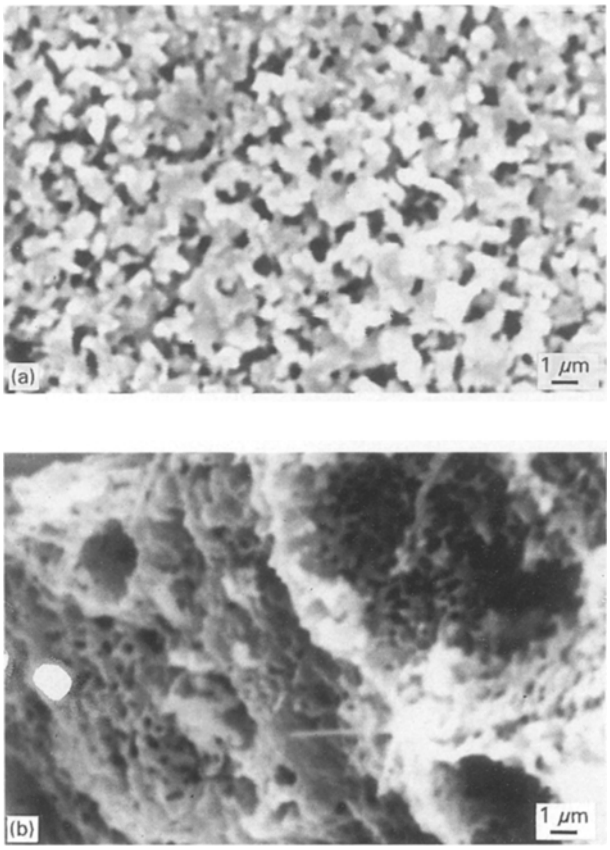

Figure 7 SEM of (a) T-2 tablets and (b) G-3 gel reacted at 1450 °C with 12 l h^{-1} N_2 flow for 14 h.

from the large mass run are shown in Fig. 6. T-2 tablets from the stable suspension with narrow pore size distribution always gave a higher degree of β′-sialon formation than for the gel derived specimens.

It should also be noted that alumina was found only in the gel derived sialon. Taking into account the previous observation that the formation of β′-sialon from these starting materials was influenced by silica evaporation, it can be stated that both broad pore size distribution as well as insufficient coal distribution caused differential silicon monoxide partial pressure inside the pores, changing the parameters of the reaction. SEM images of both gel derived and T-2 tablets reacted in the medium mass experiment are shown in Fig. 7.

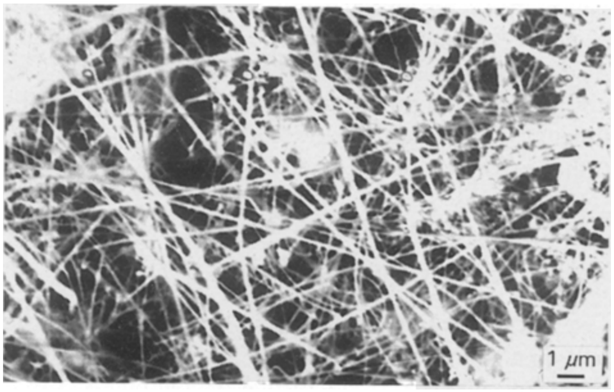

Figure 8 SEM of the condensed product formed in the medium mass run.

The medium and large mass runs were accompanied by the formation of a condensed product at the end of the reactor bed. It consisted of very fine fibres (Fig. 8). The XRD study showed that amorphous phases, as well as cristobalite and silicon carbide, were the main components of this product.

4. Discussion

The experimental findings showed that carbothermal reaction in nitrogen of a mixture of pure alumina and silica started at 1350 °C after mullite crystallization. The first step of the nitrogen involving reaction was accompanied by silicon oxynitride or O′ formation. Silicon carbide has been found only in specimens reacted at 1450 °C, and its content was nearly independent of the time of reaction.

Lee and Cutler [19] reported the formation of Si_2N_2O as a byproduct during the reaction of SiO_2 with nitrogen at 1500 °C. The formation of silicon oxynitride is described by the reaction

$$2SiO_2 + 3C + N_2 \rightarrow Si_2N_2O + 3CO \qquad (4)$$

According to the thermodynamic calculations of Bolech *et al.* [20] and Hillert *et al.* [21] Si_2N_2O should be stable above 1625–1810 K.

The authors [20] showed that carbothermal reduction of a stoichiometric mixture of silica sand and carbon black in flowing nitrogen resulted in Si_2N_2O and silicon nitride formation at 1450 °C. Addition of 1–3 wt % oxides, which form melting eutectics with SiO_2, led to significant increase of Si_2N_2O formation.

The thermodynamic equilibrium calculations performed by Tuohino *et al.* [22], in order to show the importance of partial pressures of CO and SiO for the Si_3N_4–Si_2N_2O equilibrium, allow one to see that increased partial pressures of CO and SiO favour the formation of the Si_2N_2O phase. The equilibrium boundary between the nitride and oxynitride phases lies in the area where it is quite possible to cross it, especially in the initial stage of synthesis when the reaction rate and formation of SiO and CO are high. According to these thermodynamic calculations SiC is not a stable compound under typical reaction conditions at temperatures below 1430 °C.

Other possible side reactions are

$$SiO_2 + 3C \rightarrow SiC + 2CO \qquad (5)$$

$$SiO_2 + C \rightarrow SiO + CO \qquad (6)$$

Lee and Cutler [2] and Higgins [3] suggested that the very first step of the reduction of kaolinite in nitrogen involved silicon carbide formation, which occurred independent of the nitrogen present in the system. However, they did not consider SiO evaporation. On the other hand, they found that the partial pressure of CO within the bed of pellets influenced the rate of β′-sialon formation. At low nitrogen flow, the reaction rate was dependent on the rate of removal of CO from the bed of pellets. At higher flow rates, CO pressure was maintained well below the equilibrium value, and chemical reaction rate alone determined the reaction time.

The presence of both forms of silica (amorphous and cristobalite) in the present study, as well as the high nitrogen flow ($12\ l\ h^{-1}$) compared to the total mass of the specimen (2–3 g) and SiO formation, could be the cause of the following reaction

$$6SiO_2 + 3Al_2O_3 + 15C + N_2 \rightarrow 3Al_2O_32SiO_2 + Si_2N_2O + SiC + SiO_{(g)} + 6CO_{(g)} + 9C \qquad (7)$$

The calculated and resulting phase compositions after 1 h reaction at 1450 °C are shown in Table V. This calculation is performed for the stage of the reaction where the concentrations of the intermediate mullite and Si_2N_2O reach their maxima. The observed and calculated data are in good agreement and confirm Si_2N_2O formation as intermediate. *X*-phase, reported as intermediate [3, 4, 12, 13], only at higher temperature, has not been found in the present study. It can be caused by the purity of starting materials, aluminium enrichment because of silica loss, or by the different amount of carbon applied by the authors.

β′-sialon formation in flowing N_2 involved the reaction of mullite with O′-phase in the presence of carbon. The lack of silica in the system, caused by previous SiO evaporation, resulted in AlN formation. The possible overall reaction can be written as follows:

$$3Al_2O_3 \cdot 2SiO_2 + Si_2N_2O + 9C + 4N_2 \rightarrow Si_3Al_3O_3N_5 + 3AlN + 9CO_{(g)} + SiO_2 \qquad (8)$$

TABLE V Calculated composition (wt %) from Equation 8 and resulting phase composition after 1 h reaction at 1450 °C

Phase (%)	Calculated	XRD results
Mullite	63	74
O′ phase	15	7
SiC	6	Trace
C	16	17
Mass loss	20	19

TABLE VI Calculated and resulting phase composition after 3 h reaction at 1450 °C

Phase (%)	Calculated	Observed
β′-sialon	56	56
AlN	24	20
SiC	8	6
SiO_2	12	18 (amorphous)
Mass loss	40	39

TABLE VII Calculated and resulting phase composition after 4 h reaction at 1450 °C

Phase (%)	Calculated	Observed
β′-sialon	28	30
$SiAl_4O_2N_5$ (15 R)	22	23
$SiAl_5O_2N_5$ (12 H)	13	11
Si_3N_4	7	6
AlN	10	10
SiC	8	7
SiO_2	12	13 (amorphous)

Calculated and measured data for this reaction are given in Table VI. They confirm β′-sialon formation as a result of mullite and O′-phase chemical reaction. AlN is not in equilibrium with β′-sialon, thus further reaction can be expected. One of the possible reactions can be written as follows

$$2Si_3Al_3O_3N_5 + 6AlN \rightarrow Si_3Al_3O_3N_5 + SiAl_4O_2N_4 + 0.5SiAl_5O_2N_5 + 0.5\,Si_3N_4 + 2.5AlN \qquad (9)$$

The calculated phase composition of this reaction is compared with the results after 4 h reaction in Table VII. Equation 9 implies decomposition of β′-sialon into sialon polytypoids and silicon nitride only because of equilibrium unstability of the β′-sialon–aluminium nitride system. Decomposition of β′-sialon into 15-R and AlN phases was also reported by Yoshimatsu *et al.* [13]. Cho and Charles [18] found 15-R formation as a result of β′-sialon decomposition in the presence of carbon and SiO evaporation. These results lead to the conclusion that silica losses at the very first stage of the reaction influence the quality and stability of the resulting β′-sialon.

It is known that impurities influence the formation of β′-sialon during carbothermal reduction. They increase the amount of liquid phase and cause sintering before the nitridation reaction starts and, influence mullite and cristobalite crystallization, as well as enhance β′-sialon formation.

The influence of impurities on the carbothermal reaction was not the subject of this study, but very pure starting materials employed in this project allow for comparison with a previous study. In order to minimize the influence of different factors on the reaction, Kokmeijer's [5] results carried out in the same laboratory, with the same nitrogen flow and weight of reacted specimens can be taken into consideration. After 10 h at 1400 °C or 4 h at 1500 °C Kokmeijer obtained nearly 80% β′-sialon from 42 g of starting pellets of kaolin–carbon mixture, while the same amount of β′-sialon was obtained after 14 h reaction at 1450 °C of 20 g of slip casted T-2 tablets in this study (Table IV). Moreover Kokmeijer's [5] very pure New Zealand halloysite needed 20 h at 1400 °C to be converted into 55% β′-sialon with significant amounts of β-Si_3N_4. Thus, the higher purity of starting materials strongly decreases the rate of the reaction. A similar observation was reported by [23] for Si_3N_4 formation from SiO_2.

The catalytic effect of Fe content in natural aluminio-silicates on β′-sialon formation has been reported earlier [5, 11, 24]. Less than 0.1 wt % Fe_2O_3 in the tested specimens did not prevent β′-sialon conversion, except it did decrease the reaction rate.

The other effect related to the purity of starting materials concerns silica stability during carbothermal reduction. The lack of such impurities as CaO or Fe_2O_3 slows down crystallization of cristobalite and leaves silica in the amorphous phase, less resistant to reduction to SiO.

The influence of pellet microstructure on carbothermal production of β′-sialon can be seen clearly from the results in Fig. 6. Both the good degree of mixing in slip casted T-2 tablets from the stable suspension, as well as the narrow pore size distribution, led to the β-sialon formation. Nitrogen flow through highly porous tablets with a narrow pore size distribution and homogeneous coal distribution must have ensured a similar condition for solid–gas reaction. However, if silica loss occurs, aluminium nitride and then sialon polytypoids formation is unavoidable.

5. Conclusions

1. Apart from SiC, O′-phase can occur as an intermediate in the carbothermal reaction of silica and alumina mixture in flowing nitrogen at 1450 °C.
2. A decomposition of β′-sialon can occur in the presence of AlN, leading to formation of 15-R.
3. Impurities which lead to the formation of a liquid phase increase the reaction rate.
4. It is important to control the microstructure of the pellets. A narrow pore size distribution and good homogeneity improve the yield of β′-sialon.

Acknowledgements

Partial funding for this project has been provided by the Commission of the European Communities under TEMPUS programme. The authors thank H. van der Heijde for his help and assistance.

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Received 17 December 1993
and accepted 22 June 1995