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Carbothermal reduction and nitridation of powder pyrophyllite raw material

J. Křest'an*, P. Šajgalík, Z. Pánek

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-842 36 Bratislava, Slovak Republic

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Abstract

The influence of nitrogen flow rate, temperature, time and α-Al_2O_3 addition on the carbothermal reduction and nitridation of powder pyrophyllite raw material with particle size below 60 μm has been investigated with the aim to prepare a precursor for subsequent synthesis of β-SiAlON. A fast conversion of pyrophyllite raw material to the major phase β-Si_3N_4 and two minor phases, α-Si_3N_4 and AlN, was observed at 1510 °C. The addition of fine α-Al_2O_3 to increase the amount of AlN (higher value of z) led to the considerable lengthening of the conversion time. Depending on the amount of added α-Al_2O_3, two kinds of β-SiAlON based material, containing as minor phases either $SiAl_4O_2N_4$ and α-Al_2O_3 or alone α-Al_2O_3 were prepared by hot-pressing. The same value of $z = 3.8$ was determined for all the prepared β-SiAlONs.

Keywords: Carbothermal reaction; Nitrides; Powders; Precursors; Pyrophyllite; Sialon

1. Introduction

One of the serious disadvantages, which hinder wider applications of engineering ceramics, is the high cost of the synthetic starting powder for their manufacturing. The requirements for powder quality are justified for the demanding applications, but for less stringent ones, e.g., use in metallurgy, the powder quality requirements do not have to be so strict. Many attempts were have been made to convert natural aluminosilicates, mostly kaolinite and montmorillonite based clays, to β-SiAlONs by carbothermal reduction and nitridation (CRN).[1–6] The reports related to the CRN of pyrophyllite ($Al_2Si_4O_{10}(OH)_2$) are few,[7,8] probably as a consequence of the low Al/Si ratio.

β-SiAlON ceramics ($Si_{6-z}Al_zO_zN_{8-z}$; $0 < z < 4$) may be prepared by reactive sintering of appropriate mixtures of Si_3N_4, SiO_2, Al_2O_3 and AlN powders or by sintering of β-SiAlON powder. The last method leads usually to better control of grain size and particularly stoichiometry. Therefore most of the CRN studies have focused on the preparation of β-SiAlON powders. The intimately mixed reactants and their good contact are the basic requirements, which have to be fulfilled in this case. But, despite the sophisticated homogenization and powder compaction into pellets or granules, the control of synthesis of pure β-SiAlON is difficult due to the number of successive and parallel reaction steps. Moreover, for rapid conversion, CO (g) must be effectively removed from the sample, because carbon monoxide is always on the reaction product side, e.g., for reactions (1), (2)

$$SiO_2(s) + C(s) \Longleftrightarrow SiO(g) + CO(g) \tag{1}$$

$$Al_2Si_4O_{10}(OH)_2(s) + 9\,C(s) + 3\,N_2 \Longleftrightarrow Si_4Al_2O_2N_6(s) + 9\,CO(g) + H_2O(g) \tag{2}$$

and the equilibrium constants for such reactions are small at 1400–1500 °C. Reaction (1) is generally accepted as the first reaction step during CRN of silica before Si_3N_4 or SiC forms,[9,10] depending on the temperature and nitrogen partial pressure. An analogous situation (AlN formation through aluminum suboxides), but an even smaller equilibrium constant, applies for CRN of alumina according to the equation:

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* Corresponding author.
E-mail address: jan.krestan@savba.sk (J. Křest'an).

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$$Al_2O_3(s) + 3\,C(s) + N_2(g) \Longleftrightarrow 2\,AlN(s) + 3\,CO(g) \quad (3)$$

Hence, the conversion rate and final chemical (z) and phase composition of the product prepared by CRN method will be directly influenced by nitrogen flow rate as well as by carbon particle size and content, temperature, nitrogen partial pressure, size of pellets, impurities and seeding activity.[11–13] Finally, SiAlON pellets need subsequent crushing and milling to prepare an appropriate powder.

The other possibility, as mentioned above, is the preparation of powder precursors (appropriate mixtures of oxides and nitrides) for the reactive sintering of β-SiAlONs from raw materials.

In the present work, CRN conversion of a raw material containing two major phases, pyrophyllite and quartz, was studied. The aim was to assess the possibility of raw material powder conversion into α/β-Si_3N_4, SiO_2, Al_2O_3 and AlN powder mixture without granulation or pelletizing. The high Si/Al ratio in the raw material used, which results in a low value of z and subsequently low powder sinterability, was decreased by the addition of α-Al_2O_3 powder to the pyrophyllite raw material.

2. Experimental

The powder materials used in this work were pyrophyllite (P-I, Envigeo, Ltd., Slovakia), α-Al_2O_3 (Martoxide PS-6, Martinswerk, FRG, particle size $d < 1$ μm), α-Si_3N_4 (Siconide-P, Permascand Ceramic, Sweden), β-Si_3N_4 (Tschernogolovka, Russia) and carbon black (impurities < 0.2 mass.%, $S_{BET} = 80$ m^2 g^{-1}, Stickstoffwerk Piesteritz, FRG). The chemical and mineralogical compositions of the pyrophyllite according to Envigeo Ltd. are given in Tables 1 and 2. The particle size of the pyrophyllite after grinding in an agate mortar for 0.5 h was below 60 μm (Fig. 1). The appropriate amount of dry powder materials was homogenized in a PE rotating bottle for 4 h using alumina balls. Approximately 0.15 g of homogenized powder mixture was poured into the static graphite reactor (Fig. 2), which was inserted into the graphite resistance furnace. The reactor was under vacuum up to 600 °C, above this temperature nitrogen was introduced through a diffuser into the reactor. The temperature was measured by means of a thermocouple (W5Re/W25Re) up to 1100 °C. A two color pyrometer (Ircon, USA), calibrated by the known melting temperature, of gold (1063 °C), diopside (1392 °C) and alumina (2045 °C) was used for the temperature measurement of the reactor surface above 1100 °C. The final temperature of CRN ranges from 1480 to 1510 °C with 3–8 h dwell at these temperatures. The adjusted nitrogen flow 50–300 cm^3 min^{-1} at 25 °C, controlled by means of calibrated flowmeter, corresponds approximately to a gas velocity 8–50 m min^{-1} inside the reactor at maximum temperatures. The nitrogen pressure increases from 0.1 to 0.13 MPa as the flow rate increases from 50 to 300 cm^3 min^{-1}. Products of CRN were analyzed by XRD (Stoe STADI-P, Co$K\alpha_1$) and SEM (Jeol JSM 35) methods.

Table 1
Chemical composition of pyrophyllite P-I (according Envigeo, s. r. o.)

P-I	(mass%)		(mass%)
SiO_2	78.23	MnO	0.02
TiO_2	0.59	Na_2O	0.02
Al_2O_3	15.85	K_2O	0.03
Fe_2O_3	1.65	P_2O_5	0.10
CaO	0.23	Loss of ignition	3.11
MgO	<0.01	H_2O	0.29

Table 2
Mineralogical composition of P-I

Mineral	Content (mass%)
Pyrophyllite	50–55
Quartz	40–45
Kaolinite	2–3
Hematite	2

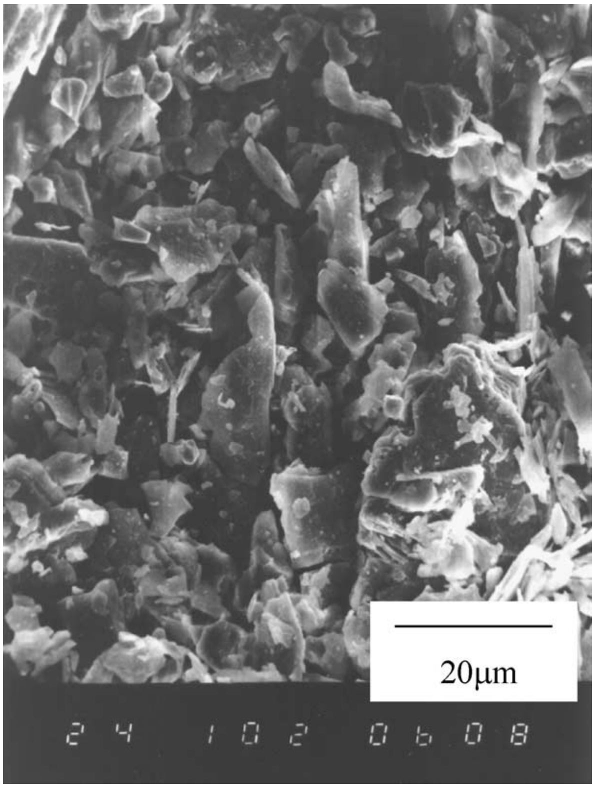

Fig. 1. SEM micrograph of pyrophyllite raw material (P-I).

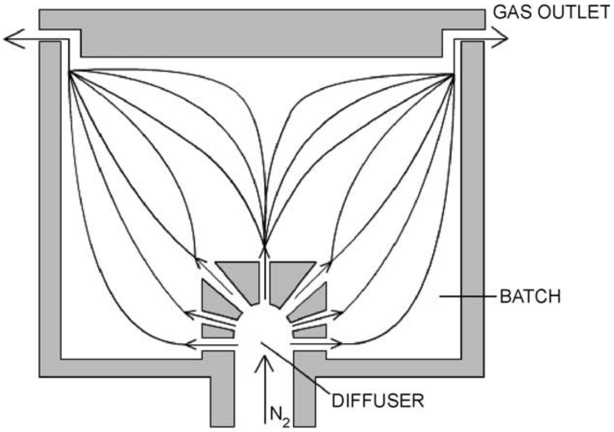

Fig. 2. Schematic drawing of reactor.

Three batches corresponding with reaction schemes (A–C) were prepared and their chemical compositions and labeling are summarized in Table 3.

$$1.386\,SiO_2 + 0.165\,Al_2O_3 + 0.979\,N_2 + 2.937\,C \Rightarrow 0.286\,Si_{4.84}Al_{1.16}O_{1.16}N_{6.84} + 2.937\,CO \quad (A)$$

$$1.386\,SiO_2 + 1.386\,Al_2O_3 + 1.386\,N_2 + 4,16\,C \Rightarrow 0.693\,Si_2Al_4O_4N_4 + 4.16\,CO \quad (B)$$

$$1.386\,SiO_2 + 0.457\,Al_2O_3 + 1.386\,N_2 + 4.143\,C \Rightarrow 0.462\,Si_3N_4 + 0,924\,AlN + 4.143\,CO \quad (C)$$

It must be emphasized here that after CRN it is not possible to expect the presence of products in accordance with the right sides of these schemes due to the kinetic aspect and change of initial composition. The (A–C) reaction schemes are considered as a base for the calculation of the theoretical composition of the starting mixture, taking into account a small amount of β-Si_3N_4 addition as a seeding which increases the conversion rate to β-Si_3N_4 see Refs. 7 and 13. For comparison the mixture D ($z=4$) was prepared from commercially available Si_3N_4, AlN and Al_2O_3 powders.

Table 3
Composition of starting mixtures

Sample	Pyrophyllite P-I (mass%)	Carbon black (mass%)	β-Si_3N_4 (mass%)	α-Al_2O_3 (mass%)	α-Si_3N_4 (mass%)	AlN (mass%)
A	69.5	23.8	6.7	–		
B	35.8	17.4	3.5	43.3		
C[a]	53.5	25.8	5.2	15.5		
D				47.9	32.9	19.2

[a] Theoretical composition corresponds to the value $z=4$ after addition of 37.7 mass% of α-Al_2O_3 to the 62.3 mass% of C after CRN.

The powder CRN products with higher z value were, as received, pressed into pellets in a steel die at 100 MPa. These pellets were hot-pressed (HP) in a graphite die in 0.1 MPa of nitrogen under a pressure of 30 MPa at 1600 and 1800 °C for 2 and 1 h, respectively. The sample D was also converted to SiAlON by pressureless reactive sintering (PLRS) in 0.1 MPa of nitrogen at 1800 °C for 1 h. The XRD method was used to analyze the samples after high temperature treatment. The z value as the mean of z_a and z_c was calculated according equations listed in Ref. 14, where the subscripts a and c indicate the z value calculated from the a and c lattice parameters of the hexagonal sialon, respectively.

3. Results and discussion

The XRD patterns of sample A after CRN at 1480 °C for 3.5 h and different nitrogen flow rate (gas velocity) are shown in Fig. 3. The highest temperature of phase equilibrium between Si_3N_4 and SiC in the presence of carbon under 0.1 MPa of nitrogen is 1515 °C.[15] Therefore, the slightly lower temperature (1480 °C) was set up for CRN to reach a high conversion rate. The formation of Si_3N_4, AlN and SiC, are thermodynamically possible in the presence of carbon at this temperature at 0.1 MPa of nitrogen. However, if the carbon is depleted, SiC reacts with nitrogen to form Si_3N_4 below 1515 °C and the released carbon reacts with oxides to form CO. The conversion degree as well as SiC formation is strongly influenced by the nitrogen flow rate (gas velocity). The degree of conversion increases and SiC content decreases as the nitrogen flow rate increases as shown in Fig. 3.

The total conversion of sample A under the described conditions was not achieved and from Fig. 3a is evident the presence of non-reacted quartz and a small amount of α-Si_3N_4. The amount of AlN and SiC is near the XRD detection limit.

The temperature was increased for the next experiments to 1510 °C to increase the conversion rate. The XRD diffraction patterns of sample A after CRN are shown in Fig. 4. The major phase was β-Si_3N_4 and minor phases were AlN, α-Si_3N_4 and SiC. The amount of quartz is at the XRD detection limit. The temperature increase of about 30 °C positively influenced the conversion rate as expected, but surprising was a relatively low SiC content regardless of the nitrogen flow rate. The single possible explanation is the temperature increase because the other parameters of CRN were identical with those at 1480 °C. Hence, the temperature slightly below the stability border of $Si_3N_4+C/SiC+N_2$ increases Si_3N_4/SiC ratio in final product. The XRD patterns of the mixture B after CRN are shown in Fig. 5.

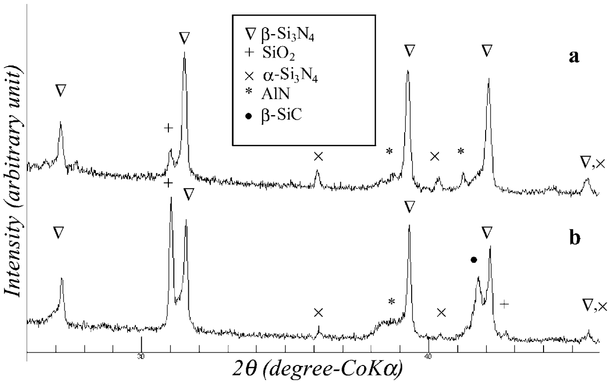

Fig. 3. Powder XRD patterns of sample A after CRN at 1480 °C for 3.5 h; a—flow rate (FR) = 50 cm^3 min^{-1}; b—FR = 300 cm^3 min^{-1}.

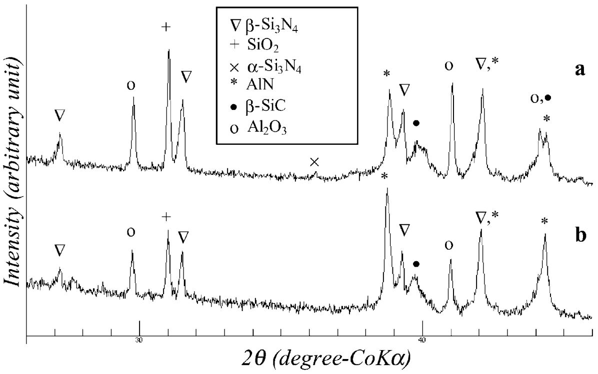

Fig. 5. Powder XRD patterns of sample B after CRN; a—1480 °C / 3.5 h, FR = 100 cm^3 min^{-1}; b—1510 °C / 3.5 h, FR = 160 cm^3 min^{-1}.

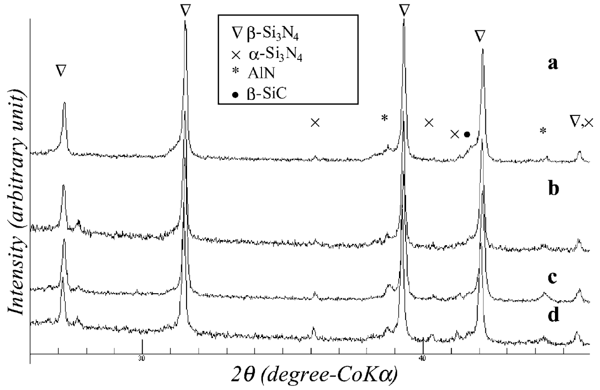

Fig. 4. Powder XRD patterns of sample A after CRN at 1510 °C for 3.5 h; a—flow rate (FR) = 50 cm^3 min^{-1}; b—FR = 100 cm^3 min^{-1}; c—FR = 200 cm^3 min^{-1}; d—FR = 300 cm^3 min^{-1}.

A high content of SiO_2 was present after conversion regardless of different CRN parameters probably due to the high content of fine α-Al_2O_3, which is converted to AlN with a higher rate comparing with the conversion of coarser silica to Si_3N_4 or SiC. The relatively high rate of AlN formation has a negative influence on SiO_2 conversion due to the increasing amount of CO and decreasing amount of N_2 in the reaction system, a situation corresponding to a lower nitrogen flow rate. That is the reason for a high content of AlN as well as of SiO_2 after CRN which subsequently led to the formation of $SiAl_4O_2N_4$ as will be discussed later. The finer pyrophyllite raw material could depress the preferential formation of AlN. The amount of SiC, if present, was below the detection limit.

The sample C has a considerably lower content of α-Al_2O_3 therefore the number of contacts between carbon and alumina particles decreases and vice-versa, the number of carbon-silica contacts increases. Hence, the better conditions for Si_3N_4 but also for SiC formation may be expected in comparison with the sample B. XRD diffraction patterns of sample C after CRN are in Fig. 6. The SEM micrograph of as prepared powder is in Fig. 7. The powder morphology and particle size were almost the same for all samples. Similarly as for sample B, the conversion of coarser SiO_2 is depressed by addition of fine α-Al_2O_3 but this influence is not so strong as in the sample B because the α-Al_2O_3 content in the sample C is substantially lower. Anyway, a considerably longer time and a high flow rate were necessary to convert almost all SiO_2 and depress the SiC content after CRN in comparison with the sample A at the same temperature. This is in accordance with similar results published by Baldo et al.,[8] that with increasing Al_2O_3, the presence of aluminosilicates increases also the conversion time. Hence, the conversion time probably increases regardless of initially chemically bonded or added alumina. The Si_3N_4/AlN ratio in sample C was considerably higher than in the sample B. The decreasing content of SiC with increasing time dwell and flow rate confirms the stability of Si_3N_4 under these conditions (1510 °C, $p_{N2} = 0.1$–0.13 MPa).

The samples B, C were hot-pressed after CRN and compared with the sample D. The composition of all these samples was calculated for $z = 4$ (assuming the initial content of SiO_2 in the pyrophyllite raw material) and their XRD patterns after HP are in Fig. 8. The sample A after CRN has not been converted into SiAlON because a low value of z, which is responsible for low possibility of densification of the as received precursor at technologically acceptable conditions. A pure SiAlON has never been achieved from these raw materials. The major phase in all samples was β-SiAlON. The minor phases were $SiAl_4O_2N_4$ and α-Al_2O_3 in sample B and only α-Al_2O_3 in sample C. This corresponds with the composition of powder samples after CRN (Figs. 5 and 6). It is reasonable to assume the simultaneous formation of SiAlON and $SiAl_4O_2N_4$ if the reaction mixture contains Si_3N_4, SiO_2, AlN and Al_2O_3. Such compounds are present in the sample B after CRN (Fig. 5). Hence, the relative high contents of AlN and SiO_2 led to the formation of considerable amount of $SiAl_4O_2N_4$ besides β-SiAlON as shown in Fig. 8a. A small amount of α-Al_2O_3 remains still non-reacted. The

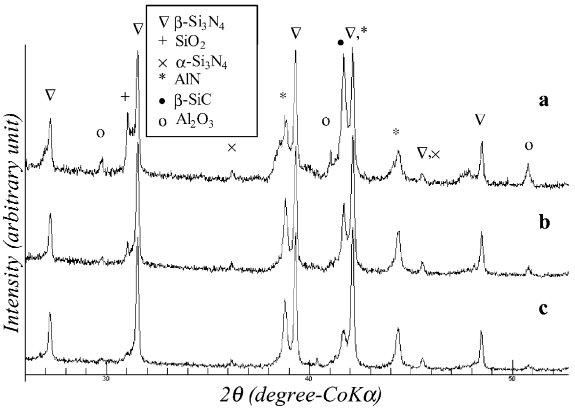

Fig. 6. Powder XRD patterns of sample C after CRN; a—1510 °C /4 h, FR = 50 cm^3 min^{-1}; b—1510 °C / 6 h, FR = 150 cm^3 min^{-1}; c—1510 °C / 8h, FR = 200 cm^3 min^{-1}.

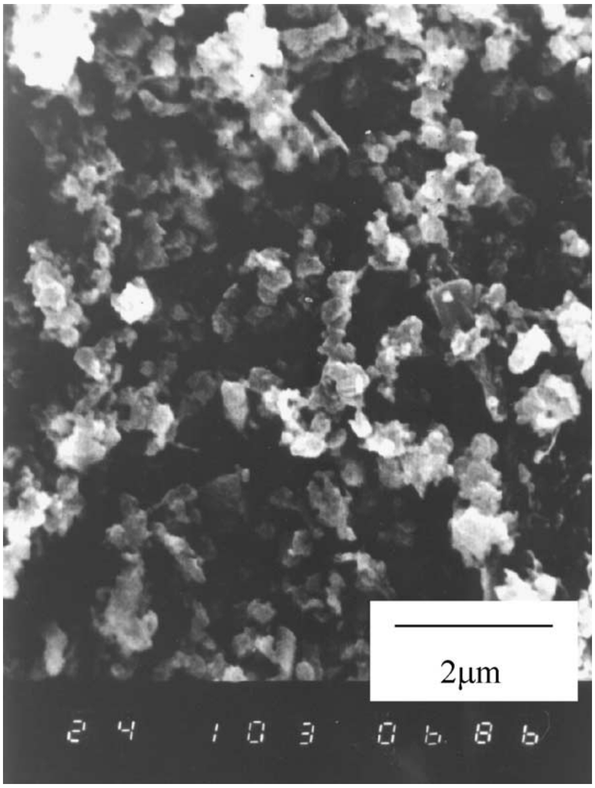

Fig. 7. SEM micrograph of sample C as received after CRN at 1510 °C / 8 h / FR = 200 cm^3 min^{-1}.

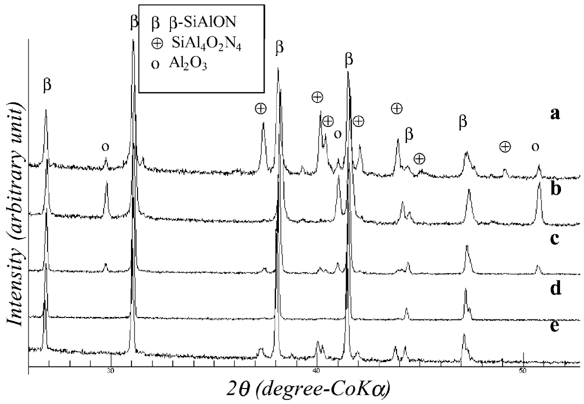

Fig. 8. Powder XRD patterns of β-SiAlONs; a—sample B, HP, 1800 °C / 1 h; b—sample C, HP, 1800 °C / 1 h; c—sample D, HP, 1600 °C / 2 h; d—sample D, HP, 1800 °C / 1 h; e—sample D, PLRS, 1800 °C / 1 h.

presence of α-Al_2O_3 after HP of samples B and C (Fig. 8b) may be explained by some mass loss of SiO_2 during the CRN in form of non-reacted SiO so that the alumina, calculated for the initial amount of SiO_2, is in an excess. The formation of SiC also contributes to this excess. The mass loss of SiO_2 depends on temperature, flow rate, reaction time and construction of reactor and it is quite difficult to eliminate this loss from the technological point of view.

A small amount of $SiAl_4O_2N_4$ and α-Al_2O_3 was determined also in sample D after HP at 1600 °C for 2 h (Fig. 8c). These minor phases disappear when the sample was hot-pressed at 1800 °C for 1 h (Fig. 8d). It means that $SiAl_4O_2N_4$ exists as an intermediate compound during the SiAlON formation independent from the composition of the starting mixture supposing the presence of some amount of SiO_2. This confirms also the presence of $SiAl_4O_2N_4$ in sample D after the pressure-less heat treatment (Fig. 8e).

The values of z 3.8 determined after final heat treatment were almost the same for all samples (B–D) suggesting the assumption of a saturated SiAlON despite the lower value of z. The more precise measurements of *d*-spacing and chemical analysis of SiAlONs should be done to explain the different phase composition but the same *d*-spacing of β-SiAlON as documented in Fig. 8c–e.

4. Conclusions

- The conversion rate during CRN of powder pyrophyllite raw material with described characteristics (sample A) depends on nitrogen flow rate or better on its velocity at 1480 °C, but this dependence was not observed at 1510 °C if the gas velocity in the reactor was equal or higher then 8 m min^{-1}.
- The formation rate of Si_3N_4 in sample A at 1480 °C increases and the amount of SiC decreases with increasing nitrogen flow rate. A sufficient conversion was not achieved neither at maximum possible gas velocity of 50 m min^{-1} after 3 h.
- The acceptable conversion of sample A was achieved during CRN at 1510 °C for 3h regardless of the nitrogen flow rate within 50–300 cm^3 min^{-1} (gas velocity inside of reactor 8–50 m

min^{-1}). The product contains β-Si_3N_4 as the major phase beside a small amount of α-Si_3N_4 and AlN and a very small amount of SiO_2 and SiC, which is on XRD detection limit.
- The addition of very fine α-Al_2O_3 to the coarser pyrophyllite raw material, to increase the value of *z*, enlarges considerably the conversion time.
- The preparation of a powder precursor from pyrophyllite raw material by CRN, which subsequently gives a β-SiAlON based material with the required phase and chemical composition depends on the temperature, time, gas velocity in the reactor, particle size of reactants and construction of reactor. All processing parameters must be optimized experimentally for a specific reactor.

Acknowledgements

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