

A modified SHS method for $\text{Si}_2\text{N}_2\text{O}$ elaboration

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Abstract

Silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) has been prepared from a compacted mixture of silicon and silica under high nitrogen gas using the high-temperature synthesis (SHS) process. The aim of this work was to optimise this reaction by using a preliminary treatment of the raw materials before the combustion. The SHS samples were characterised by using X-ray diffraction and SEM analyses. Rietveld refinement was performed on recorded diffractograms and a very high formation rate for $\text{Si}_2\text{N}_2\text{O}$ (more than 97 wt%) at low nitrogen pressure was revealed. By studying the influence of the compacting pressure, the nitrogen pressure and the reactant mixture, a mechanism of $\text{Si}_2\text{N}_2\text{O}$ formation has been suggested. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

Silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) is the unique compound in the SiO_2 – Si_3N_4 system.¹ It has a high proportion of covalent bonding, and a thermodynamic calculation of the silicon oxynitride stability indicates it to be more stable than Si_3N_4 .^{2,3} In recent years, $\text{Si}_2\text{N}_2\text{O}$ has emerged as a new high-temperature ceramic material with a variety of potential applications such as those of high-temperature electric insulator, nuclear-reactor moderator or reflector and solid electrolyte.⁴

Despite its attractive properties, a suitable synthesis technique at relatively low processing temperatures, required in silicon device technology, is still lacking. The synthesis of silicon oxynitride can be performed either through liquid phase by reaction sintering of equimolar mixtures of Si_3N_4 and SiO_2 ^{5,6} or through gas phase by nitridation of a mixture of Si and SiO_2 .^{4,7,8} Self-propagating high-temperature synthesis (SHS) seems to be an alternative route.⁹ In this

process, the strong exothermic reaction propagates spontaneously through the reactant mixture, converting it into product. Therefore, this process leads to a rapid product formation and energy efficiency.

Silicon oxynitride powder was already prepared from desert sand and silicon by using the SHS method under pressurized nitrogen gas with the presence of $\text{Si}_2\text{N}_2\text{O}$ as a diluent.⁹ Nevertheless, in addition to the main phase, a minor amount of β - Si_3N_4 was observed. According to these authors, the reaction mechanism occurs in two steps: firstly silicon is quickly combusted to silicon nitride releasing a high energy. A further reaction between the formed silicon nitride and the silica sand is then activated to synthesize stable silicon oxynitride. Thus, the presence of β - Si_3N_4 in the final product seems to be due to an incomplete reaction of $\text{Si}_2\text{N}_2\text{O}$ formation. A higher degree of contact between the surfaces of the reactants should allow increasing the conversion. The aim of this study was to optimize this reaction by using a preliminary treatment of the raw materials before the combustion reaction.

2. Experimental procedure

The influence of the contact between surfaces was studied by preparing two kinds of raw mixtures:

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- Mixture A is constituted of silicon powder (99+ wt% of Si, 0.28 wt% of Fe, 0.15 wt% of Ag and 0.11 wt% of Al, Aldrich, $-45\ \mu\text{m}$ in size) and silica powder obtained from zeosil (Rhodia). Indeed, zeosil which is an amorphous silica containing 84.96 wt% of SiO_2 , 0.9 wt% of Na_2O , 0.3 wt% of Al_2O_3 and 13.79 wt% of H_2O can give rise to porosity under a heat treatment at $120\ ^\circ\text{C}$ during 12 h. This porosity should increase the reactive surface of silica.
- Silicon powder was added to a colloidal silica solution, LUDOX HS40 (39.5 wt% of SiO_2 , 0.4 wt% of Na_2O and 60.1 wt% H_2O ; Aldrich) under stirring. This solution is then heated to evaporate water and to form mixture B. This mixture was prepared in order to optimize the surface of contact between particles.

The initial blends were characterized by means of laser granulometry (Mastersizer/E Malvern) and Leica scanning electron microscope coupled with EDX detector.

The reactant proportions in both powder mixtures were defined according to the stoichiometry of the following reaction: $3/2\ \text{Si}(\text{s}) + 1/2\ \text{SiO}_2(\text{s}) + \text{N}_2(\text{g}) \rightarrow \text{Si}_2\text{N}_2\text{O}(\text{s})$.

Green compacts were prepared from these mixtures using a uniaxial press. Two compacting pressures (P_{comp}) were studied: 100 and 300 MPa.

These compacts were placed into a furnace under high gas pressure of nitrogen (from $P_{\text{N}_2} = 2\text{--}100\ \text{MPa}$) and heated with a high speed ($90\ ^\circ\text{C}/\text{min}$). The reaction was ignited on one side of the sample and because of the existence of a thermal gradient (the furnace only consists in one heating zone) the direction of propagation for the reaction was controlled. The temperature profiles were measured by means of three thermocouples and recorded during the reaction. A schematic diagram of the SHS furnace is given on Fig. 1.

X-ray diffraction was used to characterise the SHS products. The diffraction patterns were recorded on a Phillips Expert diffractometer (with a copper $\text{K}\alpha_1$ anticathode) in the $[10\text{--}130^\circ]$ 2θ range, with a step size of 0.00836° and a step time of 500 s. The phase quantification was performed by Rietveld refinement (FULLPROF suite).^{10,11}

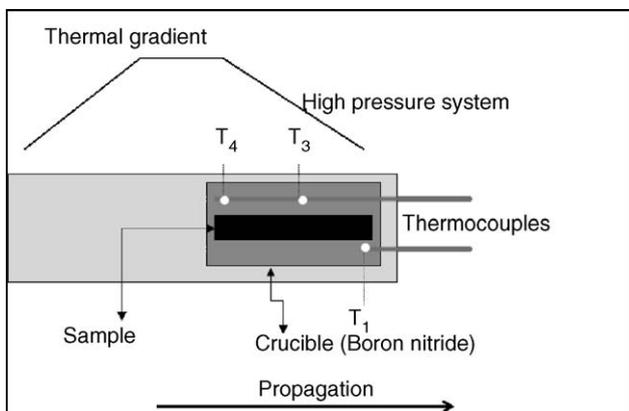


Fig. 1. Schematic diagram of the SHS furnace.

The microstructures and the composition of the SHS products were identified by a Leica scanning electron microscope coupled with an EDX detector.

3. Results

The recorded thermal profiles are used to follow the advancement of the SHS reaction. During heating, a sudden rise in temperature, corresponding to an exothermic reaction, is observed. The beginning of this phenomenon corresponds to the ignition temperature. In this work, whatever the nitrogen pressure and the studied mixture, the SHS reaction is ignited at the melting point of silicon ($T = 1416\ ^\circ\text{C}$). An example of thermal profile is given in Fig. 2. The reaction starts on the hotter side of the sample where T4 is located and the propagation of the reaction is observed along the sample by means of T3 and T1. The velocity of the reaction can also be calculated from these profiles. In this case, its value is 2.74 mm/s.

Quantitative composition of the SHS products was determined from X-ray diffractogram by Rietveld refinement (Fig. 3). Results are reported in Tables 1–4. Different crystallised phases were observed: $\text{Si}_2\text{N}_2\text{O}$, silicon, silica and extra phases (α - and β - Si_3N_4). The amorphous phases are not taken into account in this quantification.

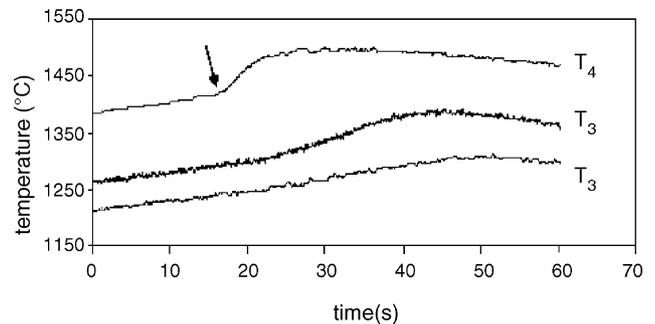


Fig. 2. Typical temperature profiles for the SHS of $\text{Si}_2\text{N}_2\text{O}$ (mixture B, $P_{\text{N}_2} = 6\ \text{MPa}$, $P_{\text{comp}} = 100\ \text{MPa}$).

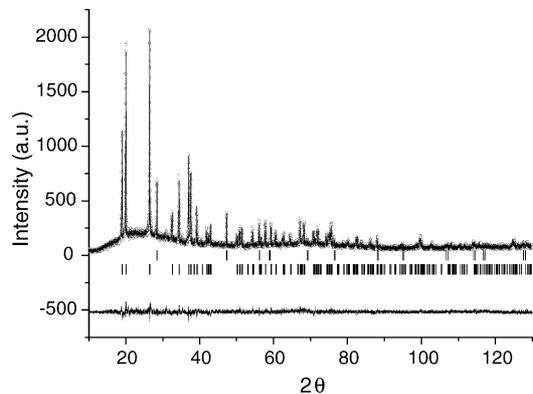


Fig. 3. Rietveld refinement for mixture B ($P_{\text{comp}} = 300\ \text{MPa}$; $P_{\text{N}_2} = 6\ \text{MPa}$). The difference between the experimental diffractogram ($^\circ$) and the calculated one (solid line) is presented in the lower part of this figure.

Table 1

Composition of the SHS samples determined by Rietveld refinement for several nitrogen pressures; mixture B ($P_{\text{comp}} = 100$ MPa)

Pressure (MPa)	Si (wt%)	Si ₂ N ₂ O (wt%)	α -Si ₃ N ₄ (wt%)	β -Si ₃ N ₄ (wt%)
2	3	97	–	–
6	4	92	4	–
20	15	66	16	3

Table 2

Composition of the SHS samples determined by Rietveld refinement for several nitrogen pressures; mixture B ($P_{\text{comp}} = 300$ MPa)

Pressure (MPa)	Si (wt%)	Si ₂ N ₂ O (wt%)	α -Si ₃ N ₄ (wt%)	β -Si ₃ N ₄ (wt%)
2	3	97	–	–
6	5	92	3	–
20	19	63	18	–
50	24	18	58	–

3.1. Influence of the compacting pressure

The influence of the compacting pressure has been studied for mixture B, results are reported in Tables 1 and 2. As the mixture was prepared in stoichiometric composition, the presence of unreacted silicon needs unreacted silica. Nevertheless, crystallised silica was not observed; therefore, it should be in an amorphous form. Indeed, amorphous phases can be observed on diffractogram, around $2\theta = 25^\circ$ (Fig. 3).

The β -Si₃N₄ phase was only evidenced for the lowest compacting pressure combined with a 20 MPa nitrogen pressure. Nevertheless, the amount of this phase, even if it is significant, is lower than 4 wt%. For the other cases, the compacting pressure has no influence on the composition of the SHS product.

3.2. Influence of the nitrogen pressure

As it was already mentioned in previous works^{12,13} because of the high thermal conductivity of the gas under pressure, the SHS reaction can be prevented. In this system, difficulties to ignite the reaction were encountered near 100 MPa.

Tables 1–3 and Fig. 4 present the weight fractions of non-reacted silicon and α -Si₃N₄ increasing with nitrogen pressure whereas the silicon oxynitride amount decreases. For the low-

est nitrogen pressure (2 MPa), the SHS products are mainly constituted of silicon oxynitride (more than 97 wt%). The extra phase is the non-reacted silicon. The presence of α -Si₃N₄ is observed from 6 to 50 MPa and its amount increases with the nitrogen pressure, up to 57 wt% at 50 MPa.

Fig. 5 shows typical SHS samples compared with the initial compact. When the nitrogen pressure is higher than 20 MPa, the transient liquid phase leads to a densification and then a reduction of the sample size. For lower pressures, the silicon oxynitride formation gives rise to significant expansions, which can even lead to powder under 2 MPa.

3.3. Influence of the reactant mixture

In order to study the influence of the type of reactant mixture, the results reported in Tables 2 and 3 are compared considering only one nitrogen pressure ($P_{\text{N}_2} = 20$ MPa) and one compacting pressure ($P_{\text{comp}} = 300$ MPa) in Table 4. The corresponding SEM micrographs and X-ray diffractograms are presented in Figs. 6–8.

For mixture A (Si + zeosil), we observed three kinds of phases: the first one corresponding to pure silicon, the second one containing silicon and nitrogen whereas the third one shows nitrogen, oxygen and silicon (Fig. 6). We can note that all the silicon grains are coated with the Si–O–N phase. Thus, we can suggest that silicon has been totally consumed when it does not appear at the core of Si–O–N phases.

Table 3

Composition of the SHS samples determined by Rietveld refinement for several nitrogen pressures; mixture A ($P_{\text{comp}} = 300$ MPa)

Pressure (MPa)	Si (wt%)	Si ₂ N ₂ O (wt%)	α -Si ₃ N ₄ (wt%)	β -Si ₃ N ₄ (wt%)	SiO ₂ (wt%)
20	18	26	49	7	–
50	30	5	54	–	11
100	39	2	48	–	12

Table 4

Composition of the SHS samples determined by Rietveld refinement for the two mixtures ($P_{\text{comp}} = 300$ MPa, $P_{\text{N}_2} = 20$ MPa)

Mixture	Si (wt%)	Si ₂ N ₂ O (wt%)	α -Si ₃ N ₄ (wt%)	β -Si ₃ N ₄ (wt%)
A	18	26	49	7
B	19	63	18	–

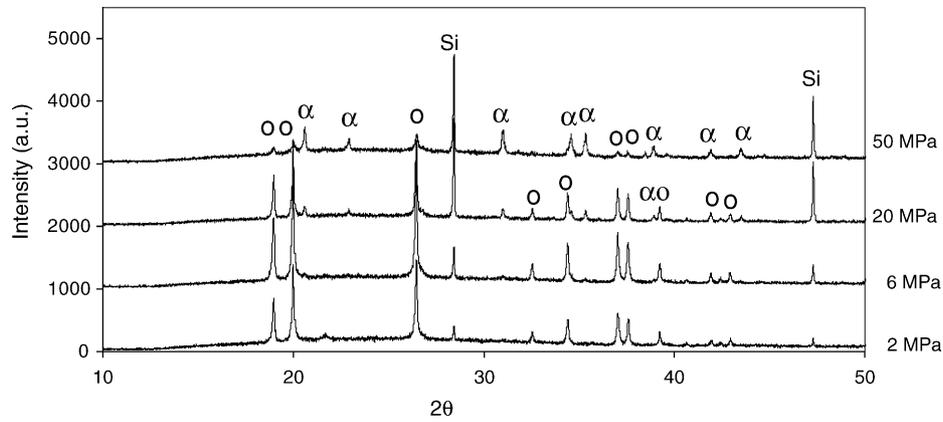


Fig. 4. Diffractograms recorded for different nitrogen pressures, mixture B ($P_{\text{comp}} = 300$ MPa). O: $\text{Si}_2\text{N}_2\text{O}$; α : $\alpha\text{-Si}_3\text{N}_4$.



Fig. 5. Photograph of SHS samples compared with the initial compact (mixture B, $P_{\text{comp}} = 300$ MPa).

For mixture B (Si + ludox), we observed the same phases as previously: Si, Si–N and Si–O–N, but with an extra one containing Si and O elements (Fig. 7). Silicon is embedded in Si–O and Si–O–N phases, whereas Si–N appears near porosity.

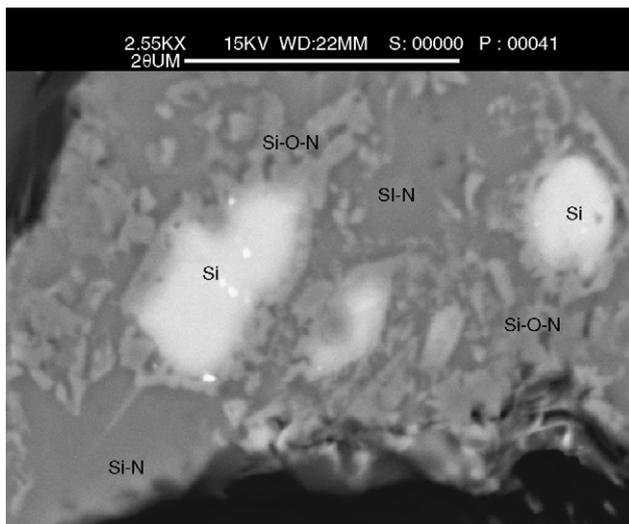


Fig. 6. SEM micrograph of mixture A ($P_{\text{comp}} = 300$ MPa, $P_{\text{N}_2} = 20$ MPa).

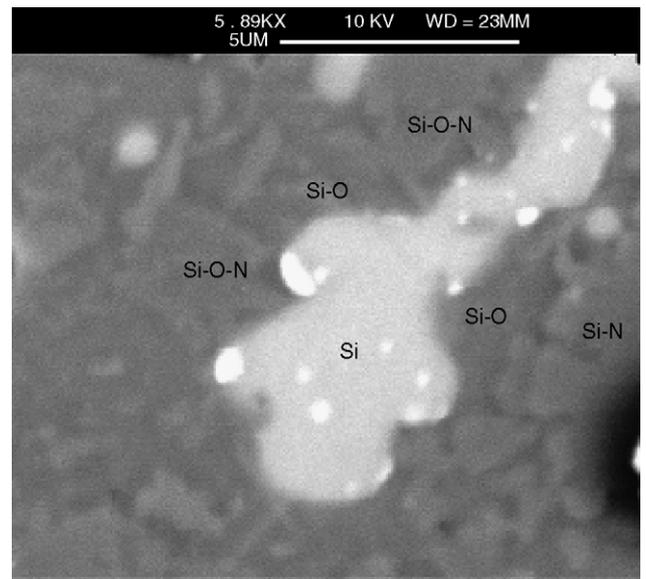


Fig. 7. SEM micrograph of mixture B ($P_{\text{comp}} = 300$ MPa, $P_{\text{N}_2} = 20$ MPa).

These results are in agreement with those obtained by X-ray diffraction (Fig. 8) and thus by quantitative refinement (Table 4). Indeed, the distinction between alpha and beta Si_3N_4 phases is impossible by SEM analyses and only

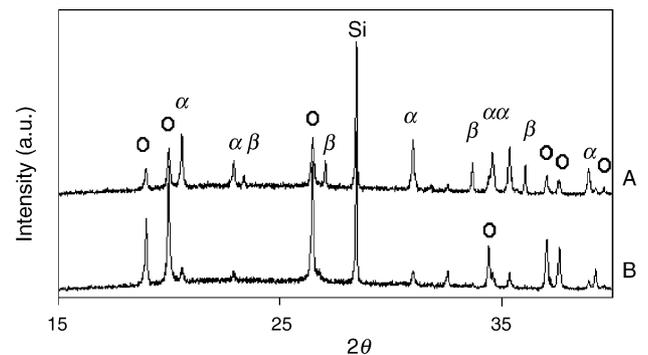


Fig. 8. Diffractograms recorded for the two mixtures A and B ($P_{\text{N}_2} = 20$ MPa). O: $\text{Si}_2\text{N}_2\text{O}$; α : $\alpha\text{-Si}_3\text{N}_4$; β : $\beta\text{-Si}_3\text{N}_4$.

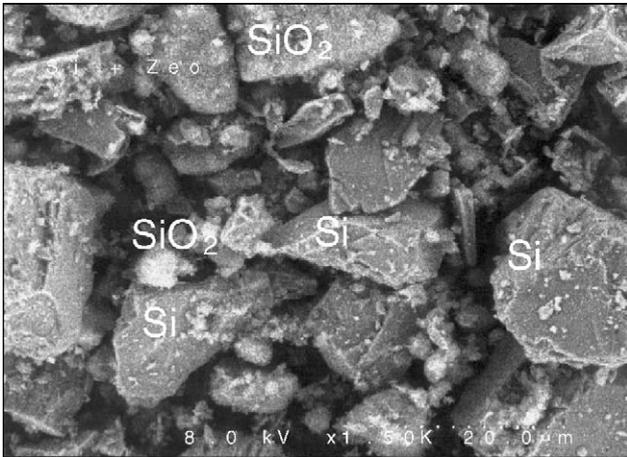


Fig. 9. SEM micrograph of raw mixture A.

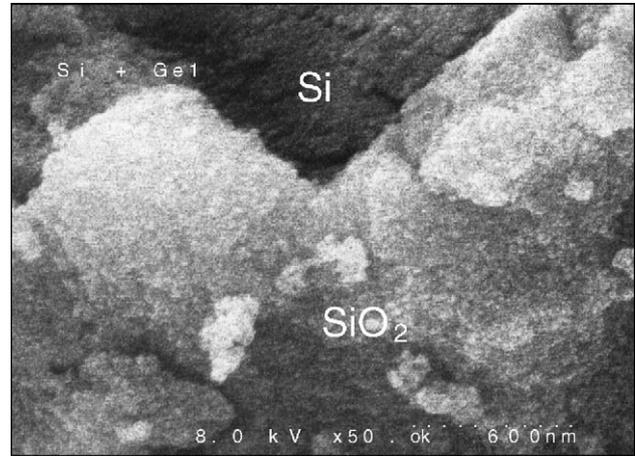


Fig. 10. SEM micrograph of raw mixture B.

a phase containing silicon and nitrogen can be determined. Furthermore, the SiO_2 phase which is not evidenced by X-ray diffraction could reasonably correspond to the phase containing Si and O in the SEM analyses.

Its absence on the diffractogram might be related to its existence under an amorphous form. The weight fraction of silicon oxynitride is higher when the reactant mixture is prepared from ludox silica.

4. Discussion and comments

This work shows that the SHS of silicon oxynitride can be improved by increasing the surface of contact between silicon and silicon oxide. Indeed, according to SEM observations of the initial powders (Figs. 9 and 10), mixture A is constituted

of two kinds of grains: Si and SiO_2 . Whereas, mixture B only contains one kind of grains, silicon grains are coated with silica. These observations have been corroborated by the grain size distribution of these mixtures. Figs. 11 and 12 give, respectively, the grain size distributions of mixtures A and B. Mixture A (zeosil + silicon) shows a bimodal distribution with two maxima, one at $10\ \mu\text{m}$ and the other at $100\ \mu\text{m}$ which, respectively, correspond to silicon and silica. Mixture B (ludox + silicon) presents a monomodal grain distribution of mean size equal to $60\ \mu\text{m}$.

When the rate of formation is high ($>97\ \text{wt}\%$), the $\beta\text{-Si}_3\text{N}_4$ phase which is reported by Radwan et al.⁹ is not evidenced (Table 2). This could result, if we consider the reactions of formation suggested by these authors, from a total conversion of $\beta\text{-Si}_3\text{N}_4$ into $\text{Si}_2\text{N}_2\text{O}$. But another explanation, which is a simpler one, could be a direct reaction between Si, SiO_2 and N_2 in the liquid phase. The formation of $\beta\text{-Si}_3\text{N}_4$ would

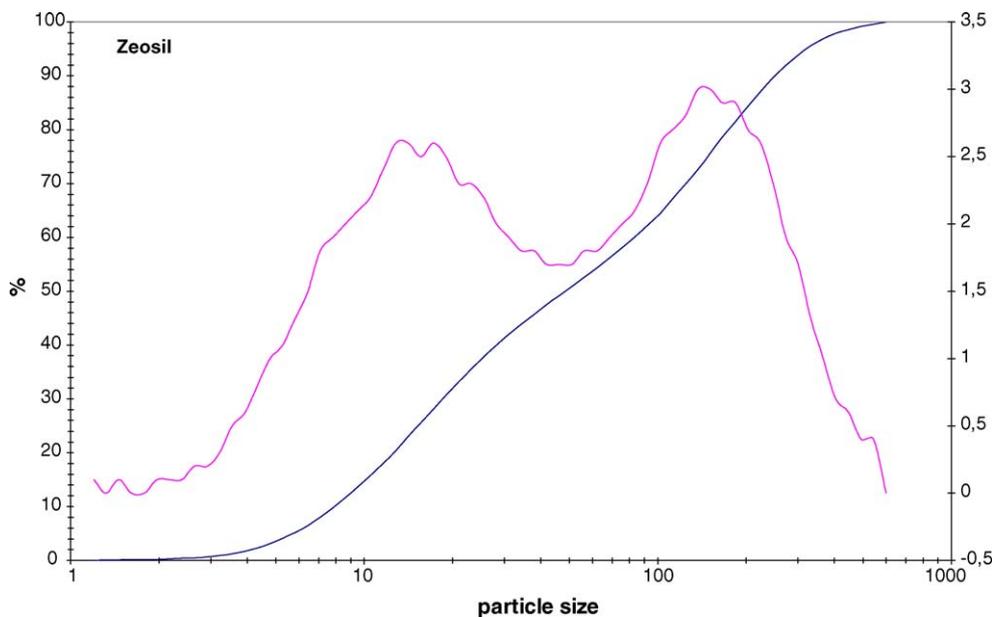


Fig. 11. Particle size distribution of mixture A powders (zeosil + silicon).

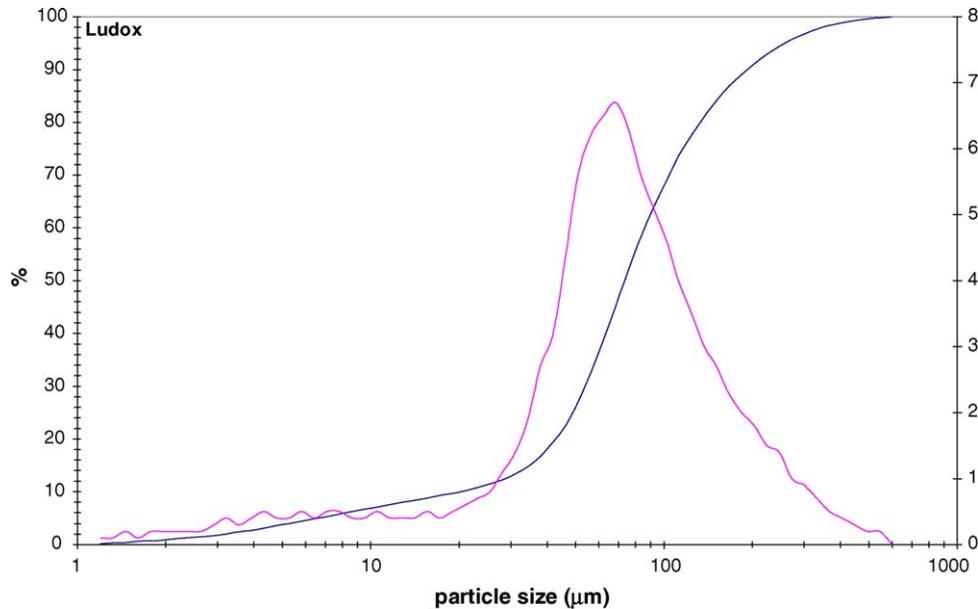


Fig. 12. Particle size distribution of mixture B powders (ludox + silicon).

be an extra reaction from silicon and nitrogen. This assumption is supported by our results. When the access of nitrogen to silicon grains is reduced, which is the case of mixture B (because of the silica coating) and when the compacting pressure is high, formation of β - Si_3N_4 is inhibited.

Therefore, depending on the accessibility of nitrogen to silicon grains, two routes are possible for the SHS reaction.

If the access of nitrogen to silicon grains is limited, silicon oxynitride can be formed. The mechanism of formation could be the following one: firstly, the molten silicon dissolves surrounding silica, then nitrogen can be incorporated in this liquid enriched in oxygen, and finally, when the stoichiometric composition is reached the silicon oxynitride is formed.

In the other case, when nitrogen can easily access to silicon, the molten silicon directly reacts with nitrogen and forms β - Si_3N_4 .

Thus, we can suggest that the SHS reactions observed in this work consist in reactions between a liquid and a gas. The liquid is generated from the melting of silicon and according to the composition of this liquid, these reactions lead to the formation of silicon oxynitride or silicon nitride.

The presence of α - Si_3N_4 could be explained by a classical mechanism of nitridation (solid–gas reaction) commonly reported in literature.^{14,15} This form should be observed at the rim of the sample. Indeed, because of the high thermal conductivity of nitrogen under pressure, this part is the coldest one and silicon cannot melt. This is in concordance with quantitative results, α - Si_3N_4 ratio increases with pressure (Table 2).

Crystallised silica was observed for mixture A, at high pressure (>50 MPa). These conditions are unfavourable to $\text{Si}_2\text{N}_2\text{O}$ formation, the reported weight fractions are very low <5 wt% (Table 3), and therefore, silica is a non reacted

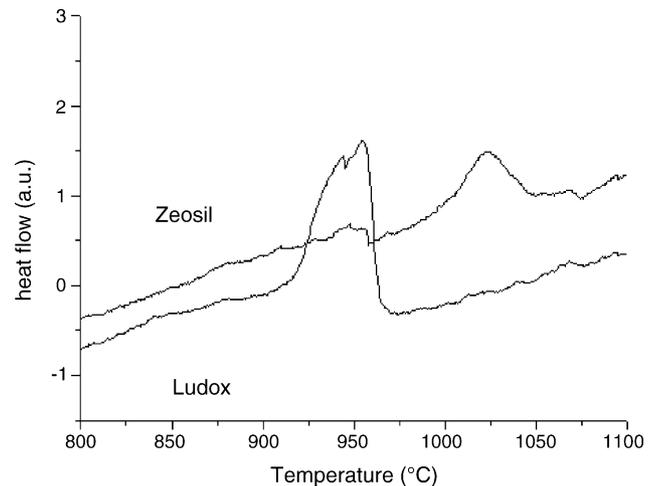


Fig. 13. DTA thermograms of raw silica (upper curve = zeosil, lower one = ludox).

one. This suggestion agrees with DTA analyses performed on the silica forms (zeosil and ludox) used in this work which crystallised, respectively, at 1020 and 950 °C (Fig. 13). The existence of this phase transformation shows that an amorphous form of silica is not required to improve the formation rate of $\text{Si}_2\text{N}_2\text{O}$. This is in agreement with Radwan, that synthesises $\text{Si}_2\text{N}_2\text{O}$ from desert sand.⁹ The most important factor is to prevent the direct reaction between silicon and nitrogen.

5. Conclusion

In the present work, silicon oxynitride has been prepared from a Si + SiO_2 mixture under nitrogen gas using SHS process. This result was previously reported by Radwan et al.⁹,

but the materials obtained so far, contained β - Si_3N_4 extra phase. Our main contribution is to point out that the formation of this latter phase can be inhibited by reducing the nitrogen access to silicon grains. A decrease of nitrogen pressure was then observed to enhance the formation of $\text{Si}_2\text{N}_2\text{O}$. Thus, pressure conditions close to atmospheric ones can be used for this synthesis. From this original result, and because of the well-known advantages of SHS, a low cost industrial process for $\text{Si}_2\text{N}_2\text{O}$ elaboration could be easily developed.

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