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Synthesis of β-SiAlON: A combined method using sol–gel and SHS processes

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Abstract

β-SiAlON has been prepared by a SHS reaction performed under high nitrogen pressure on a compacted mixture of silicon and mullite. In order to optimise this reaction, the solid mixture was prepared from a liquid solution in which the mullite ($2SiO_2$-$3Al_2O_3$) was formed by a sol–gel process. The SHS samples were characterized by using Scanning Electron Microscopy (SEM) and X-ray diffraction. A Rietveld refinement performed on the recorded diffractograms revealed a very high formation rate of β-SiAlON (more than 80 wt%) when the reaction was carried out under low nitrogen pressure. From the whole of our results, a mechanism of β-SiAlON formation has been suggested.

Keywords: β-SiAlON; SHS; Mechanism of formation; High pressure; Ceramic nitrides

1. Introduction

SiAlONs are ceramic materials based on the elements silicon, aluminium, nitrogen and oxygen. The phase diagram of the Si-Al-O-N system is well known [1,2]. Eight quaternary SiAlON phases are reported and the homogeneity range of each solid solution is precisely defined. Nevertheless, only some of them have been physically characterized: O′-SiAlON based on Si_2N_2O which can be described by the $Si_{2-z}Al_zN_{2-z}O_{1+z}$ formula with $z < 0.4$ [3]; β-SiAlON based on β-Si_3N_4 which can be described by the $Si_{6-x}Al_xO_xN_{8-x}$ formula where $0<x<4.2$ and X-SiAlON which is a line compound with the $Si_{12}Al_{18}O_{39}N_8$ composition.

Such materials possess excellent resistance to thermal shock and corrosion by molten metals. They are used for high temperature applications such as thermocouple protection sheaths in aluminium metallurgy and are candidates for hot zone parts in internal combustion engines [4].

SiAlON ceramics are prepared by either reactive sintering of Si_3N_4, Al_2O_3 and AlN powders [4,5] or by carbothermal reduction and simultaneous nitridation (CTN) of a kaolin/carbon mixture [6–8]. 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 the reaction of formation goes through a number of consecutive and parallel steps which must proceed in the appropriate rate and order to yield the desired product.

Self-propagating high-temperature synthesis (SHS) is well known as a way to elaborate high temperature materials [9,10]. 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.

The SHS has already been investigated for the elaboration of SiAlON [11,12].

The reactant mixture constituted of silicon, aluminium and oxides (SiO_2 or Al_2O_3) powders is treated under nitrogen pressure. The authors reported that the addition of Si_3N_4 or SiAlON in the reactant mixture is needed to obtain high conversion rates; the use of low nitrogen pressures (3–9 MPa [12], 2–3 MPa [11]) is also preferable. Unfortunately, the presence of additives is not desirable for an industrial transfer.

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Indeed, it increases the cost of the process: the reactant mixture is more expensive, the presence of a further phase lowers the reactant quantity and thus the product one, moreover if this further phase differs from the product, it needs to be removed at the end of the process.

The aim of this work was to re-investigate the β-SiAlON formation by SHS but without using any additive. Then, our challenge was to modify the initial conditions in order to ignite the reaction and to get high conversion rate with a product free from additional phases.

In a previous work concerning the elaboration of Si_2N_2O by SHS [13], we have shown that a higher degree of contact between the surfaces of the reactants increases the conversion. Moreover Si_2N_2O was obtained from a silicon and silica mixture under nitrogen pressure without any additive.

Therefore, we decided to use similar experimental conditions for the elaboration of SiAlON. The reactants mixture consists of silicon and mullite ($2SiO_2$-$3Al_2O_3$), after compaction it will be treated under nitrogen. In order to get silicon grains surrounded by mullite, the mixture will be prepared from a liquid solution. The mullite phase will be synthesized in situ by a sol–gel process.

2. Experimental procedure

The reactants used in our previous work [14], for the elaboration of Si_2N_2O, were silicon powder and a commercial colloidal silica solution. As we did not find this kind of solution for Mullite ($2SiO_2$-$3Al_2O_3$), we prepared it ourselves by a sol–gel method. The precursors, tetramethy orthosilicate ($Si(OCH_3)_4$, Aldrich 98%) for the silicon oxide and aluminium tri-sec butoxide ($Al(O^sBu)_3$, Aldrich 97%) for the aluminide oxide were chosen according to the literature [15,16].

A dispersion (A) and a solution (B) were prepared with the compositions given in Table 1. These compositions were chosen according to the stoichiometry of the following reaction:

$$28\,Si(s) + 2\,SiO_2\text{-}3Al_2O_3(s) + 21\,N_2(g) \rightarrow 6\,\beta\text{-}Si_5AlON_7(s) + \tfrac{7}{2}O_2(g).$$

The silicon powder (>99 wt% of Si, 0.28 wt% of Fe, 0.15 wt% of Ag and 0.11 wt% of Al) is originated from Aldrich and its grain size is lower than 45 μm.

After a total homogenisation, (A) and (B) were mixed and maintained under stirring at 150 °C for 2 h in order to remove the liquid phase. A further thermal treatment, performed at 600 °C for 1 h, led to a homogeneous powder.

Table 1
Composition of the precursors for the mullite synthesis by the sol–gel process

Dispersion A	Solution B
Acetone: 19 g Ethanoic acid: 3.13 g $Si(OCH_3)_4$: 4×10^{-3} mol Si: 56×10^{-3} mol	$Al(O^sBu)_3$: 12×10^{3} mol Diethyl ether: 5 g

The initial blends were characterized by means of laser granulometry (Mastersizer 2000-Malvern), Scanning Electron Microscopy (SEM) coupled with an EDX detector (Leica S260) and Differential Thermal Analysis (DTA).

With the SHS equipment available in our laboratory, the reaction cannot be ignited on free powders, a compaction is needed. Nevertheless, if the density is too high, the nitrogen permeation is hindered and the reaction cannot take place. Then a compromise needs to be found for choosing the compacting pressure. In this work, the compacting pressure was 300 MPa. Indeed, mechanical cohesion of the compact cannot be reached for lower pressures. In these conditions, the compact density was estimated to be 60%.

These compacts were placed into a furnace under high gas pressure of nitrogen ($P_{N_2} = 6$ and 20 MPa) and heated with a high speed (90 °C/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 (T_1, T_3, T_4) and recorded during the reaction. A schematic diagram of the SHS furnace is given in 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 $K_{\alpha 1}$ anticathode) in the (10–130°) 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) [17,18].

Morphologies and compositions of the SHS products were identified by Scanning Electron Microscopy coupled with an EDX detector (Leica S260).

3. Results

3.1. Characterization of the initial powders

The morphology of the initial powder is presented in Fig. 2. On the left hand side (lowest magnification), sharp grains with an aspect and a size similar to the silicon ones can be observed. When a higher magnification is applied (right side), these grains

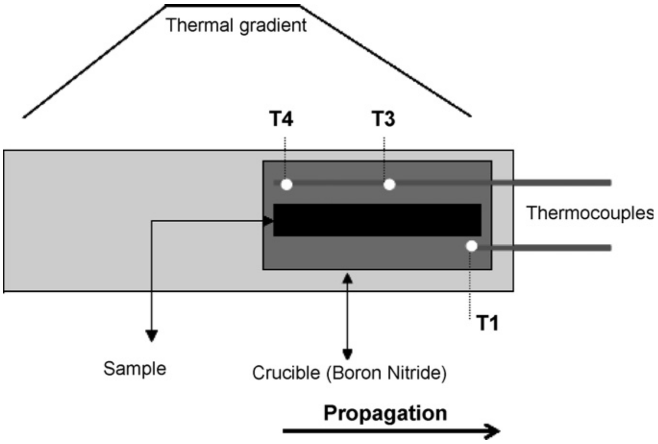

Fig. 1. Schematic diagram of the SHS furnace.

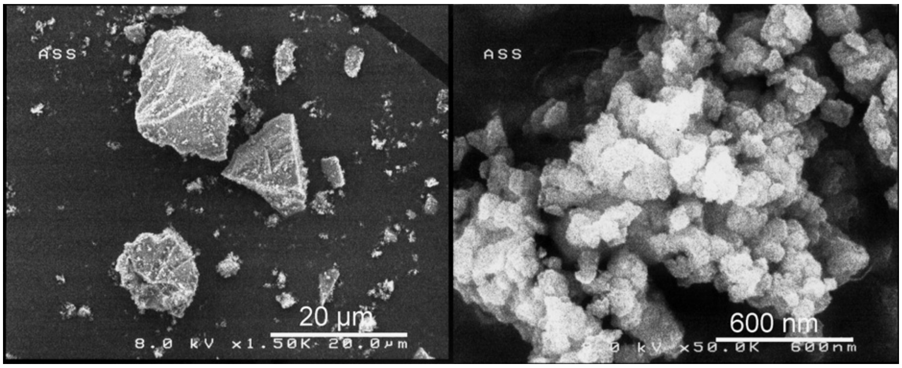

Fig. 2. SEM micrograph of the reactant mixture (left side, $G = 1500$; right side, $G = 50{,}000$).

look like an agglomeration of little ones. Therefore, we can assume from these micrographs that, because of our powder preparation, silicon grains are covered by nanometric grains of mullite.

This assumption is confirmed by the particle size measurements (Fig. 3). The grain distribution is monomodal with a mean size equal to 35 μm. This value is in agreement with the silicon grain size.

DTA measurements have been performed on this powder under argon atmosphere up to 1200 °C in order to determine its thermal behaviour. The heating rate was 10 °C/min.

The heating and cooling curves are presented in Fig. 4. An exothermic phenomenon is observed at around 1000 °C on heating. According to the literature [15,16], it could be attributed to the crystallisation of an amorphous mullite.

3.2. Thermal profiles

The thermal profiles presented in Fig. 5 were recorded at the hotter part of the compact (T_4), at the place where the reaction is ignited.

By referring to the literature results, two nitrogen pressures were considered in this work. The first one (6 MPa) belongs to a range already studied [12] and the second one (20 MPa) has been chosen higher in order to study the influence of the nitrogen pressure on the SHS reaction.

During the heating, whatever the nitrogen pressure, a rise in temperature corresponding to the exothermic reaction is observed. The ignition temperature is about 1416 °C which is the melting point of silicon. The maximum temperature decreases when the nitrogen pressure increases; its value is 1510 °C for 6 MPa and 1470 °C for 20 MPa. This difference is due to a higher thermal conductivity of nitrogen at high pressures.

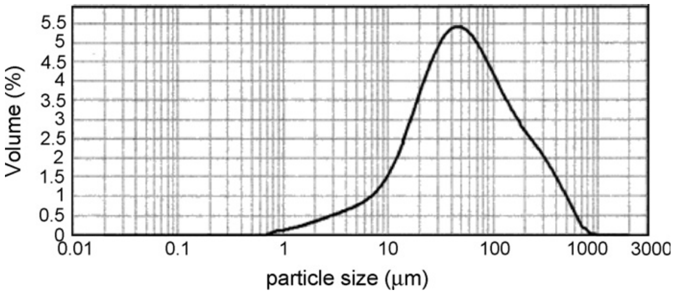

Fig. 3. Particle size distribution of the reactant mixture.

3.3. Characterization of the SHS products by X-ray diffraction

The SHS products obtained under nitrogen pressures of 6 and 20 MPa were characterized by X-ray diffraction. The diffractograms are presented in Fig. 6 and the corresponding Rietveld refinement in Fig. 7. The compositions determined by this Rietveld refinement are given in Table 2. The estimated quantities correspond only to crystalline compounds, amorphous forms were not taken into account.

Three phases have been evidenced in these samples: β-SiAlON, α-Si_3N_4 and unreacted silicon. As mullite was not found and because we can notice a slight deviation of the base line in the angular range (20–40°), we can assume that the mullite is present as an amorphous phase.

Whatever the nitrogen pressure, the quantity of unreacted silicon remains constant (around 20%). The β-SiAlON content increases when the nitrogen pressure decreases, it reaches

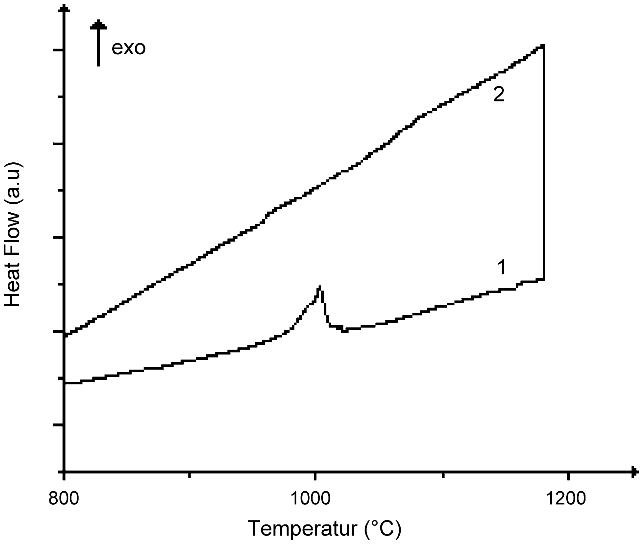

Fig. 4. DTA thermogram of mullite + silicon mixture: 1, heating; 2, cooling (upper curve).

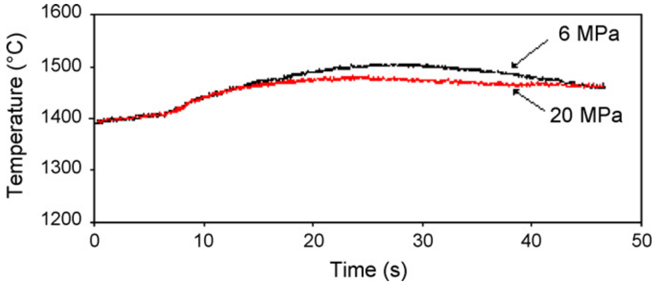

Fig. 5. Thermal profiles recorded during the SHS of β-SiAlON (P_{N_2} = 6 and 20 MPa).

79 wt% at 6 MPa. In contrast; α-Si_3N_4 only appears at 20 MPa. This phenomenon was already observed in the elaboration of Si_2N_2O [14], high pressures seem to promote the formation of α-Si_3N_4. Nevertheless, as this evolution was not noticed in the elaboration of Si_3N_4 [13], the formation of α-Si_3N_4 could also be linked to the presence of oxygen atoms in the reactant mixture. This assumption is in agreement with the literature, α-Si_3N_4 is reported in [19] as a metastable phase which can be stabilized by the presence of oxygen.

3.4. Characterization of the SHS products by Scanning Electron Microscopy

The micrographs and the EDX spectra obtained for the SHS products are, respectively, presented in Figs. 8 and 9. Whatever the nitrogen pressure, only two phases were observed: Si (light grey phase in Fig. 8, spectra a in Fig. 9) and SiAlON (mid grey phase in Fig. 8, spectra b in Fig. 9). This latter phase is more precisely β-SiAlON as it was shown by the Rietveld refinements (cf. previous paragraph).

We can also notice on these micrographs the presence of some holes (dark grey regions) which are bigger when the pressure increases.

The rounded shape of the silicon grains reveals the existence of a transient liquid and then confirms the melting of this phase.

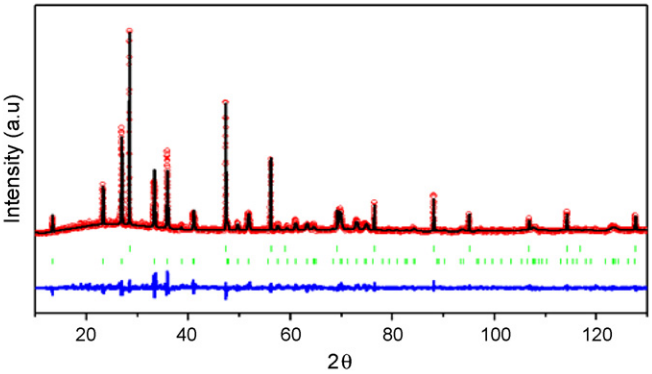

Fig. 7. Rietveld refinement for the SHS product obtained at P_{N_2} = 6 MPa. The difference between the experimental diffractogram (○) and the calculated one (solid line) is presented in the lower part of this figure.

4. Discussion

The originality of this work lies in the preparation of the starting powders using a sol–gel method. Silicon grains are then surrounded by mullite, the contact between the solid reactants is very high and the direct access of nitrogen to silicon is prevented (at least for low pressures).

Our results taken as a whole allow us to suggest the following mechanism of formation for the β-SiAlON phase by SHS:

> Firstly, when the temperature of the compact reaches 1416 °C, the silicon melts.
> Secondly, this melted silicon dissolves the surrounding mullite phase and nitrogen can be incorporated into this liquid which contains silicon, aluminium and oxygen.
> Finally, when the liquid composition corresponds to the stoichiometric one, the β-SiAlON phase is formed.

A similar mechanism was already reported in previous works on Si_3N_4 [13] and Si_2N_2O [14]. Whatever the compound, the ignition temperature is the same (1416 °C).

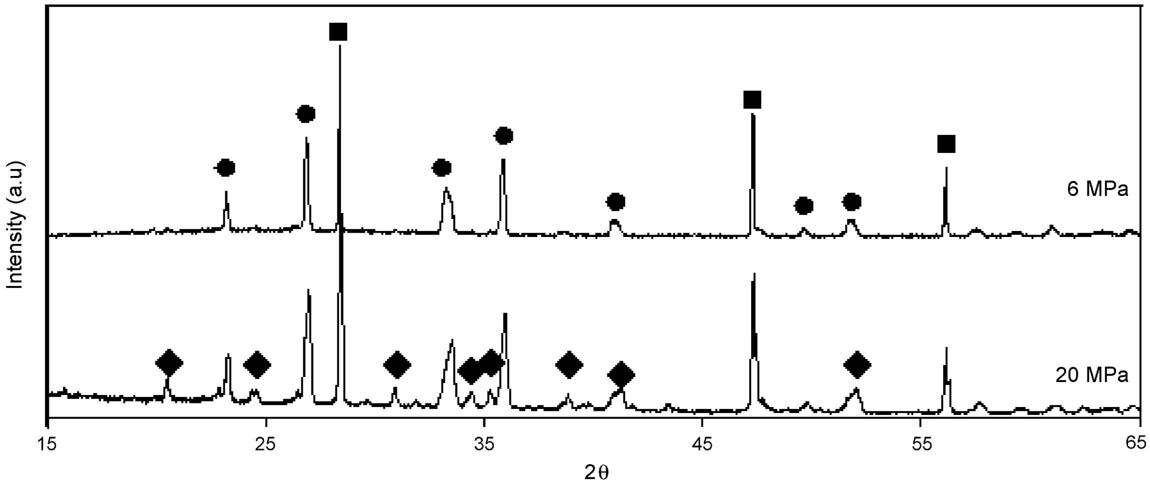

Fig. 6. Diffractograms recorded for different nitrogen pressures (P_{comp} = 300 MPa): (●) β-SiAlON; (■): Si; (◆): α-Si_3N_4.

Table 2
Composition of products obtained by Rietveld quantification for different nitrogen pressures

Pressure	Si (wt%)	β-SiAlON (wt%)	α-Si_3N_4 (wt
6 MPa	21	79	–
20 MPa	20	58	22

The melted silicon dissolves respectively Si_3N_4 and SiO_2, the nitrogen is incorporated into the liquid and when the stoichiometric composition is reached, the respective compound is formed.

Nevertheless, the corresponding thermal profiles are different. They are compared in Fig. 10 for a nitrogen pressure of 20 MPa. The Si_3N_4 profile can be distinguished from the other ones. Its maximum temperature is higher and its width is lower. At first sight, we could assume that this difference is linked to the preparation of the reactant powders. Indeed, for Si_2N_2O and β-SiAlON, the reactant powders were prepared from a liquid solution. However as it was reported above in this paper and in [13], at high pressure, α-Si_3N_4 has also been evidenced in the SHS products for both Si_2N_2O and β-SiAlON. Thus we can assume that, in these conditions, a further reaction takes place directly between liquid silicon and nitrogen.

The direct contact between nitrogen and liquid silicon is made possible by the use of a high nitrogen pressure which breaks the coating of silica or mullite. This extra reaction is also an exothermic one and it takes place before the total dissolution of silica or mullite.

Thus at 20 MPa, whatever the studied compound, the reactions involved are similar and the differences on the thermal profile rather seem to be linked to the dissolution process of nitride silicon, silica and mullite into the melted silicon. The width is linked to the dissolution kinetic and the maximum temperature to the dissolution energy. As expected, silica and mullite which are related oxides show a similar behaviour. These assumptions need to be verified but at high temperatures (>1400 °C), the melted silicon is very reactive and experiments are almost impossible.

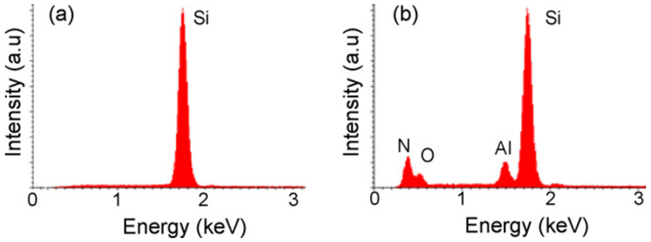

Fig. 9. EDS spectra corresponding to the analysis of the Fig. 8: (a) light phases and (b) dark phases.

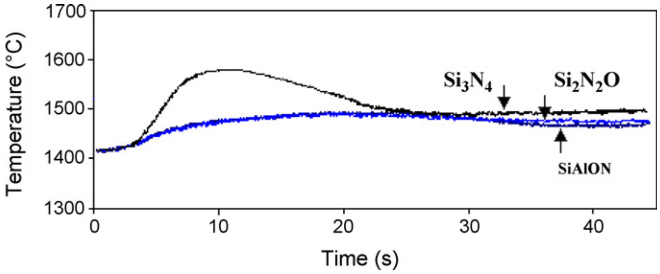

Fig. 10. Comparison between the thermal profiles recorded during the SHS of Si_3N_4, Si_2N_2O and SiAlON ($P_{N_2} = 20\,\text{MPa}$).

The presence of an amorphous mullite assumed from the X-ray diffractograms could be originated from the high cooling rate (50 °C/min) of the SHS samples.

In contrast to the literature, β-SiAlON has been synthesized in this work without additive. Usually additives are used to decrease the maximum temperature of reaction and/or to separate the silicon grains in order to improve their reactivity in the liquid state. This is well confirmed by our present work in which silicon grains are also separated from one another. However, the advantage of our procedure is that silicon grains are completely surrounded by the mullite phase and the direct reaction between nitrogen and silicon is hindered. Thus a higher conversion rate has been reached (79 wt% at 6 MPa) and no extra phase has been evidenced in the SHS product obtained under low nitrogen pressure.

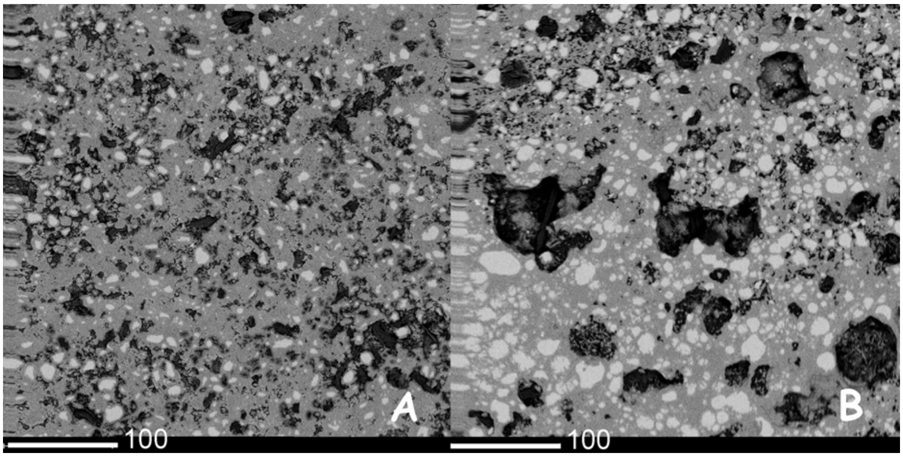

Fig. 8. SEM micrographs of the SHS products obtained at 6 MPa (A) and 20 MPa (B) (×250).

5. Conclusion

The β-SiAlON has been synthesized from a silicon and mullite mixture under high nitrogen pressure using the SHS process. This reaction has been already studied in literature but the main contribution of this work is to show that additives are not necessary to reach high conversion rates and that it is possible to obtain pure β-SiAlON without any extra phase.

From the whole of our results, a mechanism of formation for the β-SiAlON phase by SHS has also been suggested.

The originality of this work lies in the preparation of the starting powders by using a sol–gel method. Silicon grains are then surrounded by the mullite phase, the contact between the solid reactants is very high and the direct access of nitrogen to silicon is prevented (at least for low pressures).

In addition to the advantages of the usual SHS process (low cost and rapidity, $t \approx 40$ s) the possibility to prepare pure β-SiAlON without using additive, with a high conversion rate and under low nitrogen pressure makes this sol–gel/SHS process very interesting for an industrial application. Other quaternary phases of the Si-Al-O-N system could also be synthesized by this original process.

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