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# Influence of thermal conditions on the combustion synthesis of $Si_2N_2O$ phase

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# Abstract

This work is a contribution to the study of  $Si_2N_2O$  synthesis via Self-Propagating High-temperature Synthesis (SHS).

The elaboration of  $Si_2N_2O$  was carried out using two kinds of experimental equipments and differences both in reaction temperatures and in products compositions were evidenced.

In order to determine the reaction mechanisms, several compositions and thermal conditions of the reactant mixture were studied. Considering our results, two kinds of reaction mechanisms for the combustion synthesis of Si<sub>2</sub>N<sub>2</sub>O could be suggested. Furthermore, the results previously reported in the literature have been explained in the light of this work.

The SHS samples were characterized by X-ray diffraction and scanning electron microscopy (SEM) analysis. Their quantitative compositions were determined by Rietveld refinement.

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# 1. Introduction

Silicon oxynitride  $(Si_2N_2O)$  is the unique compound in the  $SiO_2-Si_3N_4$  quasi-binary [1]. Like  $Si_3N_4$ ,  $Si_2N_2O$  is a refractory material which exhibits good thermal, chemical and mechanical stability, as well as diffusive barrier and dielectric properties [2].

However, while  $Si_3N_4$  can be encountered at room temperature and atmospheric pressure in two crystalline forms ( $\alpha$  and  $\beta$ ),  $Si_2N_2O$  is a compound with a well-defined composition and structure [3]. Therefore, its constitution is constant and the improvement and/or the control of its mechanical and electrical properties must be easier than for  $Si_3N_4$  [4,5].

The synthesis of silicon oxynitride is usually performed by reactive sintering of a  $Si_3N_4$  and  $SiO_2$  mixture in the presence of a liquid phase obtained by the addition of  $Al_2O_3$  or  $Y_2O_3$  [6,7]. Nevertheless, because the additives are still present in the product of this reaction, other routes have been investigated: nitridation of high purity silica in ammonia

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at 1120 °C [8] and Self-Propagating High-temperature Synthesis (SHS) from desert sand and silicon mixture under nitrogen pressure [9]. In the first case, the formation of Si<sub>2</sub>N<sub>2</sub>O always goes along with the formation of undesirable phases: Si<sub>3</sub>N<sub>4</sub>, SiN<sub>3</sub>O and SiN<sub>2</sub>O<sub>2</sub>. In the SHS product, a further phase  $\beta$ -Si<sub>3</sub>N<sub>4</sub> is also evidenced though in a minor amount.

Therefore, the Self-propagating High-temperature Synthesis seems to be a good alternative.

In this process, a strong exothermic reaction propagates spontaneously through the reactant mixture, converting it into product.

Recently, some of us [10] have also investigated the elaboration of Si<sub>2</sub>N<sub>2</sub>O from a Si + SiO<sub>2</sub> mixture under nitrogen pressure using the SHS process. However, in this case, the SHS device was not a conventional one. The product of the reaction was constituted of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>,  $\beta$ -Si<sub>3</sub>N<sub>4</sub> and residual silicon; Si<sub>2</sub>N<sub>2</sub>O was not observed. The only way to get Si<sub>2</sub>N<sub>2</sub>O with this kind of apparatus was to use colloidal silica as raw material. The rate of formation was then very high (97 wt.% at  $P_{N_2} = 2$  MPa) and no extra phase was found in the SHS product.

The objective of this work was to understand the combustion synthesis of  $Si_2N_2O$  with two kinds of apparatus in order to explain the differences between the results previously reported [9,10]. In this aim, we studied the influence of the SHS device and more generally of the thermal conditions on the formation of  $Si_2N_2O$ .

This work results from an international collaboration between the LPMC Laboratory (Laboratoire de Physicochimie de la Matiere Condensee, Universite Montpellier II, France) and the ISMAN Institute (Institute of Structural Macrokinetics and Materials Science, Chernogolovka, Russia).

## 2. Experimental procedure

#### 2.1. Experimental devices

Two kinds of SHS device were used in this study; they mainly differ by the ignition system and the thermal conditions.

## 2.1.1. LPMC device

In the LPMC device, the reactant mixture is compacted, then placed into a furnace under a high nitrogen pressure and heated at a high speed. The crucible which contains the compact is boron nitride.

Because of the existence of a thermal gradient (the furnace only consists in one heating zone), the reaction is ignited on one side of the sample and its direction of propagation is controlled. The temperature profiles are determined 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.

The compacting pressure ( $P_{\rm comp} = 300$  MPa) and the heating rate (90 °C/min) have been selected in order to get both the ignition and the complete propagation of the SHS reaction. If these experimental parameters are too low (for the heating rate) or too high (for the compacting pressure), thermal losses are higher than the provided energy and the reaction cannot be ignited. The nitrogen pressure ( $P_{\rm N_2} = 2$  MPa) has been selected to be in the same order of magnitude as the nitrogen pressure used by Radwan et al. [9].



Fig. 1. Schematic diagram of the SHS furnace (LPMC).

# 2.1.2. ISMAN device

In the ISMAN device, the reactant mixture is used without compaction at room temperature.

It is placed into a container filled with boron nitride powder to minimize heat losses. The reaction ignition, under high nitrogen pressure, of the top of the sample is mediated by the combustion of titanium powder. A tungsten spiral heated by electric current is used to initiate titanium powder combustion. The temperature is determined by means of two thermocouples WRe5/WRe20 of 0.2 mm in diameter. This device is presented on Fig. 2.

The value of 10 MPa for the nitrogen pressure was also selected in this case in order to compare all the results.

## 2.2. Green mixtures

In our previous work [10], it was shown that the reaction of formation of  $Si_2N_2O$  can be optimised with a better contact between the reactant powders. Therefore, the present study was carried out using four kinds of raw mixtures. The reactant proportions in all these mixtures were defined according to the stoichiometry of the following reaction:

 $\frac{3}{2}$ Si(s) +  $\frac{1}{2}$ SiO<sub>2</sub>(s) + N<sub>2</sub>(g)  $\rightarrow$  Si<sub>2</sub>N<sub>2</sub>O(s).

# 2.2.1. LPMC device

- The first one (labelled A LPMC) was constituted of silicon (>99 wt.% of Si, 0.28 wt.% of Fe, 0.15 wt.% of Ag, and 0.11 wt.% of Al, Aldrich,  $-45 \mu m$  in size) and silica (Fontainebleau sand, 260  $\mu m$ ) powders. In order to improve the reactivity of the reactant mixture, the Fontainebleau sand was ball-milled for 15 h.
- The second one (labelled B LPMC) was prepared using a colloidal silica solution LUDOX HS40 (39.5 wt.% of SiO<sub>2</sub>, 0.4 wt.% of Na<sub>2</sub>O and 60.1 wt.% H<sub>2</sub>O, Dupont Chemical). Silicon powder was added to the LUDOX silica under stirring. After a total homogenisation (45 min), this solution was heated (70–80 °C) to remove the liquid phase. And a further thermal treatment, performed at 110 °C for 2 h, led to a homogeneous powder.

# 2.2.2. ISMAN device

- The third one (labelled A ISMAN) has the same composition as the first green mixture (A LPMC). It is constituted of crystalline silicon and silica. However, its preparation was realized from ISMAN's powders by mixing them into a planetary ball-milling machine during 7 min.
- The fourth one (labelled B ISMAN), contains, like the mixture B LPMC, silicon powder and amorphous silica. But the preparation is also different in this case. It was made from ISMAN powders, the amorphous silica was heat



Fig. 2. Schematic diagram of the SHS device (ISMAN).

treated at 600  $^{\circ}$ C in order to increase the specific surface, and the mixture was prepared into a planetary ball-milling machine during 7 min.

# 2.3. Methods of characterization

The starting materials were characterized by means of laser granulometry (Mastersizer 2000-Malvern), scanning electron microscopy (SEM) coupled with an EDX detector (Leica S260), gas adsorption (BET) and differential thermal analysis (DTA).

X-ray diffraction was used to characterize the SHS products. The diffraction patterns were recorded on a Phillips Expert diffractometer (with a copper K  $\alpha_1$  anticathode) in the [10–130°]  $2\theta$  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) [11,12].

Morphologies and compositions of the SHS products were identified by scanning electron microscopy coupled with an EDX detector (Leica S260).

# 3. Results and discussion

#### 3.1. Characterization of the starting materials

#### 3.1.1. Mixture A LPMC (Si + Fontainebleau sand)

In the original Fontainebleau sand, the grains are round shaped with a mean size approximately equal to  $260 \,\mu\text{m}$ . After the ball-milling, the grain size is reduced to  $8.4 \,\mu\text{m}$ .

The BET specific surface areas measured for the silicon, the original Fontainebleau sand and the ball-milled one are given in Table 1. As expected, the specific surface area of the sand is higher after milling.

The DTA profile recorded for this mixture under argon up to 1200  $^{\circ}$ C is presented on Fig. 3. An endothermic transformation is observed at 575  $^{\circ}$ C on the heating curve. This phenomenon which is reversible could correspond to the phase transition between low quartz (rhombohedral) and high quartz (hexagonal) [13]. This result is in agreement with the X-ray diffractograms recorded before and after the differential thermal analysis. In both cases, the silica is crystalline with a low quartz structure.

#### 3.1.2. Mixture B LPMC $(Si + SiO_2 LUDOX)$

The grain distribution of this mixture is monomodal with a mean size equal to 50  $\mu$ m (Fig. 4). This result is in agreement with SEM observations which present silicon grains surrounded by silica (Fig. 5).

The DTA profile recorded for this mixture under argon up to 1200 °C is presented on Fig. 6.

An exothermic phenomenon is observed on the heating curve at 950 °C. Since the cooling curve does not show any endothermic event, this phenomenon is not reversible. Therefore, we assume that it corresponds to the crystallization of an amorphous silica phase. The exothermic phenomenon observed at 210 °C on the cooling curve might correspond to the phase transition between high and low cristobalite [13].

Specific surface areas (DET) of the reactants in ETTTE and Tottini ( Inixtures					
Reactant	Specific surface area (m <sup>2</sup> /g)	Average size of particles (µm)			
LPMC powders					
Silicon	0.921	_			
Fontainebleau sand	0.025	260			
Milled sand	1.830	8.4			
ISMAN powders					
Silicon	4.2	1.12			
Milled quartz	0.6	5.04			
Amorphous silica	310	-			

Specific surface areas (BET) of the reactants in LPMC and ISMAN mixtures

Table 1



Fig. 3. DTA thermogram of Fontainebleau sand: (1) heating; (2) cooling.



Fig. 4. Particle size distribution of the reactant mixture B (LPMC).

The X-ray diffractograms recorded before and after the DTA corroborate these assumptions (Fig. 7): crystalline silica is only present after the DTA (b), it is evidenced as cristobalite. A slight deviation of the base line in the angular range  $[20-40^{\circ}]$  can be noticed on the diffractogram recorded before DTA (a).

The BET specific surface area of this mixture B is relatively high; it amounts to  $109 \text{ m}^2/\text{g}$ .



Fig. 5. SEM micrograph of the reactant mixture B (LPMC).



Fig. 6. DTA thermogram of the reactant mixture B: (1) heating; (2) cooling (LPMC).



Fig. 7. X-ray diffractograms of the reactant mixture B: (a) before DTA, (b) after DTA.

## 3.1.3. Mixture A and B ISMAN

The characteristics of the ISMAN powders are given in Table 1. For mixture B ISMAN, the specific surface of silica is 266 m<sup>2</sup>/g before the heat treatment at 600 °C and 310 m<sup>2</sup>/g after that. It is still amorphous after the heat treatment.

# 3.2. Combustion synthesis

# 3.2.1. LPMC device

When the studied mixture was constituted of silicon and Fontainebleau sand (grain size =  $8.4 \mu m$ ), the reaction was ignited and propagated all along the sample. The corresponding thermal profiles are depicted in Fig. 8. The ignition temperature is 1416 °C that corresponds to the melting point of silicon. The maximum temperature is around 1500 °C. The duration of the phenomenon is approximately 20 s.



Fig. 8. Thermal profiles recorded for the reactant mixture A (LPMC device).



Fig. 9. Thermal profiles recorded for the reactant mixture B (ISMAN device).

For the mixture B LPMC, the thermal profiles have similar shapes to the previous ones. The reaction is also ignited at the melting point of silicon but in this case the maximum temperature is slightly lower (1485  $^{\circ}$ C) than the previous one and the duration of the phenomenon is slightly longer (35 s).

#### 3.2.2. ISMAN device

For the mixture A ISMAN the reaction is ignited and propagated all along the sample. The corresponding thermal profiles are depicted in Fig. 9. The maximum temperature is around 2000 °C, very close to the maximum temperature reported in the elaboration of the silicon nitride [14] with the same kind of SHS device.

The speed of combustion in the ISMAN device (0.3 mm/s) is much lower than the speed reported for the LPMC apparatus (2.6 mm/s). This difference could be due to the preheating of the sample in the latter device.

The mixture B ISMAN was also ignited. The thermal profiles have similar shapes to the previous ones. The maximum temperature is almost the same, but combustion velocity is 1.1 mm/s.

Table 2 compares the velocity of combustion and the maximum temperature obtained with each kind of device. The LPMC device leads to a lower maximum temperature and a higher velocity of combustion. The mixture B LPMC was also studied with the ISMAN apparatus, but the reaction could not be ignited.

# 3.3. Characterization of the SHS samples

#### 3.3.1. Reactant mixture (A) (LPMC, ISMAN)

The results of the Rietveld refinement are given in Table 3. When the ISMAN device is used, the SHS product is made of  $Si_2N_2O$ ,  $\alpha$ - $Si_3N_4$  and  $\beta$ - $Si_3N_4$ . No residual silicon was observed.

With the LPMC device, the SHS samples contain  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>,  $\beta$ -Si<sub>3</sub>N<sub>4</sub> and residual silicon.

Table 2 Velocity of combustion and maximum temperature obtained from reactant mixtures A and B

Device	Velocity of combustion (mm/s)	Maximum temperature (°C)	
A (ISMAN)	0.3	2160	
A (LPMC)	2.6	1520	
B (ISMAN)	1.1	2133	
B (LPMC)	2.0	1485	

Composition of the SHS products (from mixture A and mixture B) determined by Rietveld refinement ( $P_{N_2} = 10 \text{ MPa}$ )						
Device	Si (wt.%)	Si <sub>2</sub> N <sub>2</sub> O (wt.%)	$\alpha$ -Si <sub>3</sub> N <sub>4</sub> (wt.%)	$\beta$ -Si <sub>3</sub> N <sub>4</sub> (wt.%)		
Mixture A						
LPMC	29	_	36	35		
ISMAN	-	43	27	30		
Mixture B						
LPMC	5	92	3	_		

55

3

11.5

26

2000 1500 Intensity (a.u) 1000 500 0 40 50 90 10 20 30 60 70 80 100 110 120 130 **2**0

Fig. 10. X-ray diffractogram of an SHS product from mixture B (LPMC).

#### 3.3.2. Reactant mixture (B) (LPMC, ISMAN)

5

7.5

The results of the Rietveld refinement are given in Table 3. The SHS product obtained with the LPMC device is constituted of Si<sub>2</sub>N<sub>2</sub>O,  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>, and residual silicon. As the silica phase has not been evidenced and because we can notice a slight deviation of the base line in the angular range  $[20-40^\circ]$  (Fig. 10), we can assume that this phase is not crystallized but is present in an amorphous form.

The ISMAN product contains  $Si_2N_2O$ ,  $\alpha$ - $Si_3N_4$ ,  $\beta$ - $Si_3N_4$  and residual silicon. Once more, we can notice a slight deviation of the base line in the angular range  $[20-40^{\circ}]$  and no silica in the SHS product. Therefore, the residual silica might be in an amorphous form.

# 4. Mechanisms of formation

Table 4

Main results of this study

The main results of this study are summarized in Table 4. They clearly show that the percentage of  $Si_2N_2O$ , the velocity of combustion, the ignition and the maximum temperature depend on the device. Therefore, we can reasonably assume that the mechanism of reaction differs from one apparatus to another.

Considering our results, we can suggest the following mechanisms.

With the LPMC device, the reaction is ignited at the melting point of silicon.

For the mixture A, nitrogen can easily reach the silicon grains, then it can be dissolved into the melted silicon and when the composition of the liquid corresponds to the stoichiometry of  $Si_3N_4$ , the reaction takes place that yields this

Han results of this study							
Device	Mixture	Velocity of combustion (mm/s)	Ignition temperature (°C)	Maximum temperature (°C)	Si <sub>2</sub> N <sub>2</sub> O (wt.%)		
LPMC	В	2.0	1416	1485	92		
ISMAN	В	1.1	_	2133	55		
LPMC	А	2.6	1416	1520	0		
ISMAN	А	0.3	-	2160	43		

Table 3

ISMAN

compound. As it was previously suggested for the elaboration of  $Si_3N_4$  [15], this reaction might lead to the formation of  $\beta$ -Si<sub>3</sub>N<sub>4</sub>.  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> might be the product of a direct nitridation which takes place in the coldest part of the compact. Indeed, this phase was evidenced at the rim of the sample.

The SHS samples are then constituted of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>,  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, residual Si and amorphous SiO<sub>2</sub>.

In the mixture B, the nitrogen cannot reach the silicon grains. When silicon melts, it dissolves silica which surrounds it and comes in contact with the nitrogen gas. Then this liquid containing silicon and oxygen dissolves nitrogen and when the stoichiometry is reached, the formation of  $Si_2N_2O$  occurs. This phenomenon of dissolution results in a wider thermal profile.

The presence of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> is also evidenced in this case. It was previously reported that the direct reaction between silicon and nitrogen is made possible by the use of a high nitrogen pressure which breaks the coating of silica. At lower pressure ( $P_{N_2} = 2 \text{ MPa}$ ), only Si<sub>2</sub>N<sub>2</sub>O, residual silicon and amorphous silica were evidenced in the SHS product [10]. The maximum temperature is around 1500 °C in both cases.

With the ISMAN device, the reactant powders are heated from room temperature at a very high speed  $(10^2-10^3 \text{ K/s})$ . Therefore, we can assume that in these conditions silicon is sublimed instead of being melted. This assumption is corroborated by the fact that the reaction was not ignited with this apparatus when the silicon grains are surrounded by silica (mixture B LPMC).

Thus, the sudden rise in temperature appearing in the thermal profiles is due to a highly exothermic reaction which takes place between gaseous silicon and nitrogen. Part of the released energy is then used to melt the remaining solid silicon which could not be sublimed so far and this liquid can either react with nitrogen to form  $\beta$ -Si<sub>3</sub>N<sub>4</sub> or dissolve silica to subsequently react with nitrogen to form Si<sub>2</sub>N<sub>2</sub>O.

The mechanism of formation of  $Si_2N_2O$  by SHS has never been studied so far. The results available from literature only concern the elaboration of  $Si_3N_4$  in a conventional SHS device. Two kinds of mechanism have been suggested: according to Mukasyan and Borovinskaya [16], nitrogen reacts with silicon by a vapour–liquid–crystal (VLC) mechanism; by contrast, according to Ge et al. [17], nitrogen reacts with gaseous silicon.

The mechanism suggested in this work combines these two kinds of reaction with nitrogen dissolution into the melted silicon. As shown in Fig. 11, the thermal profiles can be considered as the superposition of two phenomena: the first one (a) corresponds to a highly exothermic reaction between nitrogen and gaseous silicon, and the second one (b) corresponds to the reaction between nitrogen and melted silicon.

The previously reported results on the combustion synthesis of  $Si_2N_2O$  [9] can be explained by our suggestion. The maximum temperature reached by this system is around 1500 °C, and only two phases have been evidenced in the SHS product, namely  $Si_2N_2O$  and  $\beta$ -Si<sub>3</sub>N<sub>4</sub>.

If  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> does not appear, we can assume that the reaction between gaseous silicon and nitrogen does not occur. Indeed it seems difficult for silicon to be sublimed with the configuration used in this study. The SHS device is a conventional one but the ignition system is located at the bottom of the crucible (between the crucible and the powders).



Fig. 11. Decomposition of a thermal profile recorded on the ISMAN device. (a curve) Reaction between  $N_2$  and Si(g); (b curve) reaction between  $N_2$  and Si(l).

Without this highly exothermic reaction, the maximum temperature might not reach 2000 °C, in contrast to the ISMAN device.

Nevertheless, the silicon was melted and could react directly or after the silica dissolution with nitrogen, leading respectively to  $\beta$ -Si<sub>3</sub>N<sub>4</sub> and Si<sub>2</sub>N<sub>2</sub>O. These reactions were possible because a refractory compound (Si<sub>2</sub>N<sub>2</sub>O) was added to the mixture, and because of the location of the ignition system, the heat losses were reduced.

The low amount of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> can be explained by a preliminary ball milling (for 2 h) of the reactant powders. As with the mixture B in the LPMC device, the direct reaction between liquid silicon and nitrogen was prevented by a better contact between the reactant powders.

# 5. Conclusion

The objective of this work was to explain the differences observed between previously reported results [9,10] on combustion synthesis of  $Si_2N_2O$ . Because these differences seemed to be due to the experimental conditions, an international collaboration between the LPMC laboratory (France) and the ISMAN institute (Russia) has been established in order to carry out comparative investigations using two different kinds of SHS devices. These apparatus mainly differ by the ignition system and the thermal conditions.

Our results allowed us to understand the reactions occurring within both two kinds of apparatus during the combustion synthesis of  $Si_2N_2O$ . Furthermore, the results previously reported in the literature have been explained in the light of this work.

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