Journal of the European Ceramic Society 21 (2001) 291–295
www.elsevier.com/locate/jeurceramsoc

Self-propagating high temperature-synthesis of Si_3N_4: role of ammonium salt addition

I.G. Cano *, S. Pérez Baelo, M.A. Rodríguez, S. de Aza

Instituto de Cerámica y Vidrio (CSIC), Anta. Crta. Valencia km. 23,400, 28500 Arganda del Rey, Madrid, Spain

Received 26 February 2000; received in revised form 12 May 2000; accepted 26 May 2000

Abstract

This paper presents results of combustion synthesis (SHS) of Si_3N_4 from silicon powders under nitrogen pressure ($P_{\text{nitrogen}} = 10$ MPa). The role of different additives, such as NH_4Cl, NH_4F, $NH_4CO_2NH_2$, $(NH_4)_2\ C_2O_4H_2O$, $NH_3\ CO_3H + NH_2COONH_4$, on Si_3N_4 synthesis has been examined. Density and microstructural variations have been studied too. The product as synthesised presents two very different types of morphologies; (1) agglomerated form of α-Si_3N_4 and β-Si_3N_4, and (2) irregular formations with presence of oxynitrides and other phases. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Powders-solid state reaction; SHS; Si_3N_4; Whiskers

1. Introduction

The main obstacle for a wider use of Si_3N_4-based materials is the cost of their synthesis and final processing. Direct nitridation, carbothermal reduction,[1,2] vapour phase reactions[3] and thermal decomposition[4] are the most commonly used processes. These synthesis techniques usually require high energy contributions during long periods of time and the production rates are very low, therefore, the high production cost.

It is well known that many materials are obtained using the technique of self-propagating high-temperature synthesis (SHS),[5] originally developed in the former USSR.[6–8] This technique has also been applied successfully to silicon nitridation in nitrogen atmosphere. The SHS process is started by provoking an exothermic reaction in an area of the reactant mixture. Once initiated, there is sufficient heat release for the reaction to become self-propagating and a combustion wave travels along the reactants, converting them to the final products. The nitridation of silicon powders takes place in a self-sustained regime when high-pressures [9–11] and a dilution of silicon reagent with fine powders of Si_3N_4 are used. Combustion characteristics include high combustion front rates (10^{-4}–10^{-3} m/s), generation of high temperatures (1700–2000°C) and rapid heating (10^3–10^4 K/s). Due to relatively fast cooling rates solid products consisting of no equilibrium phases might also be formed.

Comparing the SHS technique with the conventional synthesis methods of Si_3N_4, it presents big advantages such us great energy efficiency, high purity of the products and a high production rate.[12] Many studies exist about synthesis of Si_3N_4 by means of SHS and their reaction mechanism[13,14] but there are still some problems to be solved before achieving a good and controlled production process.

As it was previously described, the combustion of Si_3N_4 in nitrogen atmosphere[15–17] presents high reaction speeds and, therefore, the microstructural control is difficult. Besides, the combustion temperatures are very high and silicon particles melt in the combustion front and coalesce during reaction, which inhibits complete nitridation. In fact to avoid this effect Si_3N_4 is incorporated as a diluent and sometimes ammonium salts are added in the initial mixture (generally ammonium halides such us NH_4Cl and NH_4F) to improve the process.[18–21] These salts generally sublime to relatively low temperatures producing a fluffiness effect, which improves the nitridation process. Most of the research agree that mainly Si_3N_4 with a high content in β-phase is formed during the silicon nitridation by SHS,[10]

---

* Corresponding author. Tel.: +34-1-871-1800; fax: +34-1-870-0550.
E-mail address: ireneg@icv.csic.es (I.G. Cano).

PII: S0955-2219(00)00168-0

however, the bibliography of patents indicates that an addition of ammonium and metal halides can promote the α-phase formation.[22]

From a technological point of view the use of ammonium salts produces corrosion inside as well as outside the reactors. Treating residual gases is needed due to environmental aspects and, therefore, it is interesting to study the possibility of using those salts whose residuals are easily recyclable. This work tries to carry out a first approach in this way, comparing the effects caused by the addition of salts from organic and inorganic acids.

2. Experimental

The main characteristics of the used raw materials were:

1. Metallic silicon powders with a purity >99%, average particle size of 4 μm and specific surface 3.37 m^2/g
2. Nitrogen from Alphagaz-Airliquide, type N-50 B-50, impurities < 3 ppm; $O_2 < 2$ ppm; $C_nH_m < 0.1$ ppm; $CO < 0.5$ ppm; $H_2 < 1$ ppm.
3. Si_3N_4 powders obtained by SHS in the laboratory with a size particle average 30 μm and the following composition (weight percentages): 16.7% α-phase, 77.2%β- phase and 6.1% free silicon.
4. Salts: ammonium chloride (NH_4Cl, Merck, purity >98%); ammonium fluoride (NH_4F, Merck, purity >98%); ammonium carbamato (NH_4CO_2 NH_2, Merck, purity > 99.5%); ammonium oxalate (($NH_4)_2$ $C_2O_4{\cdot}H_2O$, Merck, purity >99.5%); ammonium acetate (CH_3COONH_4, Merck, purity >98%) and ammonium carbonate (NH_3 $CO_3H+NH_2COONH_4$, PANREAC, purity >99%)

Table 1
Compositions and nomenclature of the mixtures

Diluent (mol%) Salt (mol%)	0	5
5% NH_4Cl	SN 1a	SN 2a
5% NH_4F	SN 1b	SN 2b
5% Ammonium carbamate	SN 1c	SN 2c
5% Ammonium oxalate	SN 1d	SN 2d
5% Ammonium acetate	SN 1e	SN 2e
5% Ammonium carbonate	SN 1f	SN 2f
Diluent (mol%)	5	20
Without salt	SN 2	SN 3

The compositions of the different mixtures (detailed in the Table 1) were formulated maintaining the quantity of silicon constant in all experiments. Diluent and additives percentages have been given referring to silicon concentration in the mixture. Likewise these percentages are expressed in mol, more explicit from a chemical point of view.

The synthesis reactor was 2 l in volume and 100 mm. in diameter. The powders homogeneously blended were placed on a graphite support along half of the reactor length. The ignition was carried out in an end of the reactor using an electric resistance of Ni:Cr that was activated inside a mixture of Ti:C 1/1 mol%. The initial nitrogen pressure in all the experiences was 10 MPa.

Quantitative analysis of present phases after synthesis was determined by X-ray diffraction (Siemens D-5000) and calculated according to Gazzara and Messier.[23] Morphologies were observed by scanning electronic microscopy (C. Zeiss, DSM-950) and, densities were calculated by mercury picnometry to atmospheric pressure (Micromeritics, Pore sizer- 9300).

3. Results and discussion

In compositions with salts added, the maximum pressures reached during the process around 13–14 MPa and a bit lower (12 MPa) when diluent was incorporated to the mixture. This phenomenon seems logical if we consider that the increase of the pressure during the reaction will be affected by the contribution of the own nitrogen and that of the generated gases in the combustion. This last contribution depends totally on whether ammonium salts are added or not. It has also been observed that the speeds in the experiments run without salts are lower, what it makes suppose that this addition can influence the reaction mechanism.

Table 2
Phases composition

Salts (5 mol%)	Si (35 g)	Si (35 g) + 5 mol% Si_3N_4
–	–	$Si_3N_4(\alpha+\beta)+Si$
NH_4Cl	$Si_3N_4(\alpha+\beta)$	$Si_3N_4(\alpha+\beta)+Si$
NH_4F	$Si_3N_4(\alpha+\beta)$	$Si_3N_4(\alpha+\beta)+Si$
$NH_4CO_2NH_2$	$Si_3N_4(\alpha+\beta)+Si_2ON_2+Si$	$Si_3N_4(\alpha+\beta)+Si_2ON_2+Si+SiC$?
$(NH_4)_2$ $C_2O_4{\cdot}H_2O$	$Si_3N_4(\alpha+\beta)+Si_2ON_2+Si+SiC$?	$Si_3N_4(\alpha+\beta)+Si_2ON_2+Si+SiC$?
CH_3COONH_4	$Si_3N_4(\alpha+\beta)+Si_2ON_2+Si+SiC$?	$Si_3N_4(\alpha+\beta)+Si_2ON_2+Si+SiC$?
NH_3 $CO_3H+NH_2COONH_4$	$Si_3N_4(\alpha+\beta)+Si_2ON_2+Si+SiC$?	$Si_3N_4(\alpha+\beta)+Si_2ON_2+Si+SiC$?

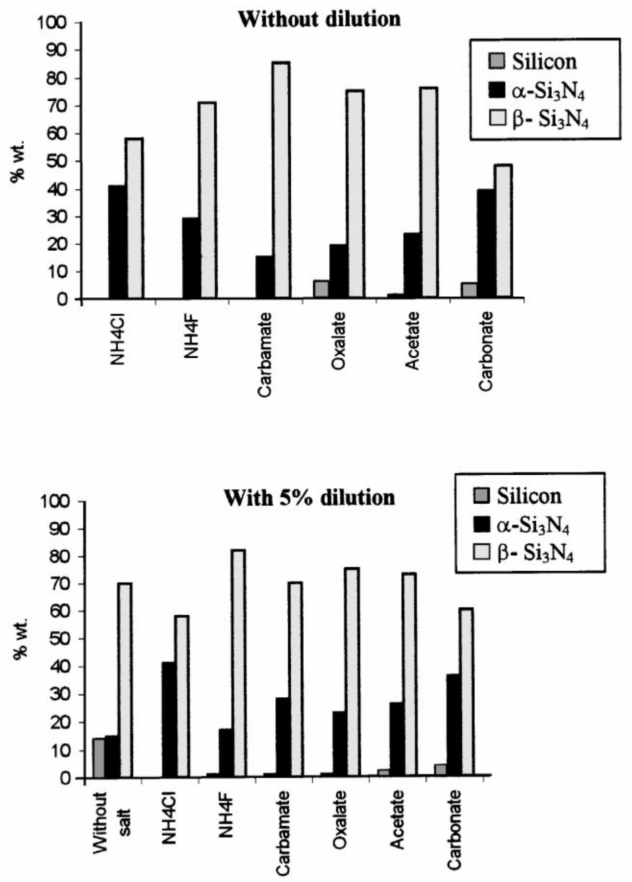

Fig. 1. Free silicon and α-Si_3N_4 and β- Si_3N_4 contents.

Table 3
Results of densities and relation between β-phase and α-phase

	Si (35 g)		Si (35 g) + 5 mol% Si_3N_4	
Ammonium salts (5 mol%)	β/α	Densities	β/α	Densities
–			4.66	1.3
Chloride	1.41	0.5	1.41	0.5
Fluoride	2.45	0.7	4.82	0.6
Carbamate	5.66	0.5	2.5	0.6
Oxalate	3.95	0.7	3.26	0.8
Acetate	3.30	0.6	2.8	0.6
Carbonate	1.23	0.7	1.66	0.6

Qualitatively through DRX, the existence of different phases has been observed, (phase composition are shown in Table 2). It is important to note the presence of oxynitrides in the cases where addition of organic salts was made, this phenomenon is due to presence of oxygen in the mixture. However, when ammonium fluoride and chloride salts are added, the identified products were only α-Si_3N_4, β-Si_3N_4 and non-reacted silicon although in these cases the disadvantageous presence of undesirable residual gases (hydrochloric and hydrofluoric acids) was founded. Non-reacted silicon appeared in all the cases except for those where there is not diluent in the initial mixture although these silicon percentages (Fig. 1) are not so high. Only a considerable increase is observed with no incorporation of salts (*SN 2*). This highlights the importance of the additives to facilitate and favour the nitridation. Small amounts of SiC have been identified too.

Quantitatively moderate differences are observed between the α-Si_3N_4 and β-Si_3N_4 contents through all the experiments. Comparing the cases of highest or lowest generation of phases α-Si_3N_4 and β-Si_3N_4 (Table 3), a bigger α-Si_3N_4 synthesis was observed with the addition of the salts and, particularly with the use of ammonium chloride and carbonate. It was also seen that the reaction level only decreases lightly with the dilution degree while increases with the salts addition.

Density measures were made in comparable parts of the samples. In the results (Table 3) it is possible to clearly observe how the porosity of the sample increases considerably with the salts addition. This increase is due to the fluffiness caused by gasses generation in the reactive mixture during the combustion. The fluffiness improves the accessibility from the nitrogen to the silicon reagent. The generation of ammoniac gases affects to the nitridation of the silicon mechanism,[17,18,24] but not significantly to the density of the sample.

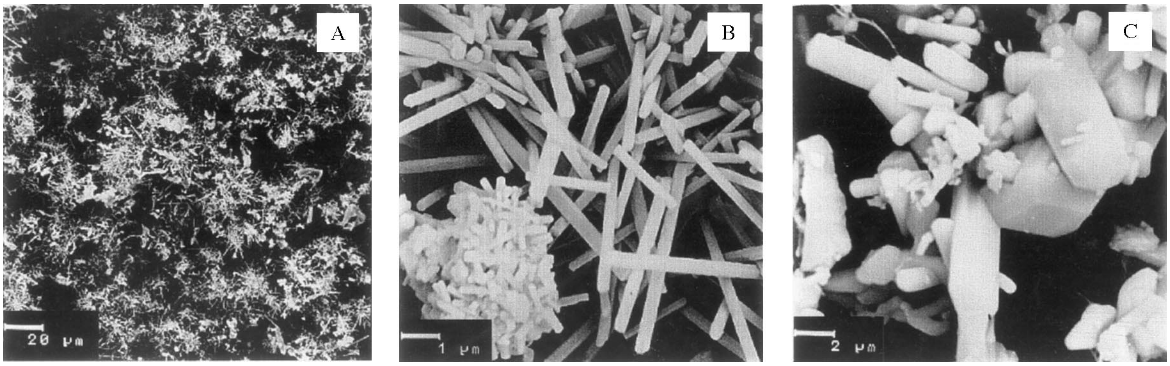

Fig. 2. Micrographics corresponding to reaction with salts of NH_4F and NH_4Cl: (A) and (B) NH_4F without dilution; (C) NH_4Cl without dilution.

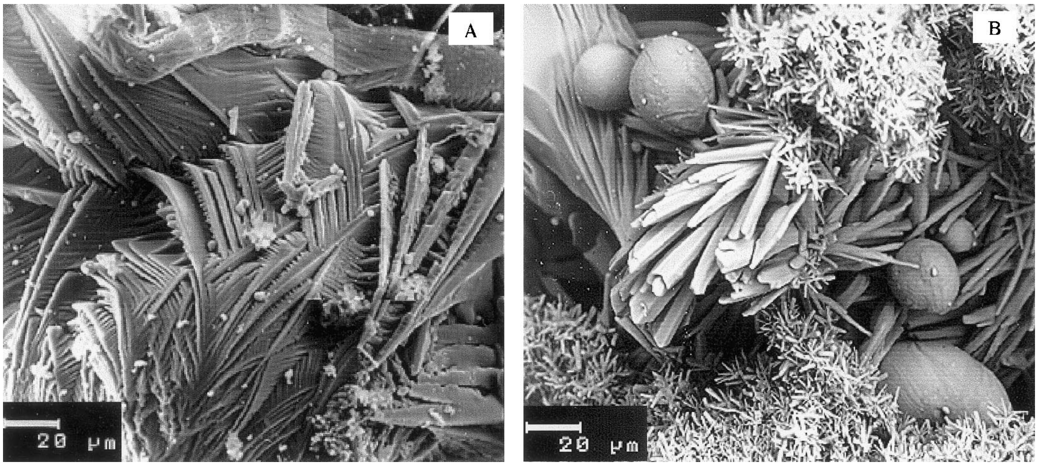

Fig. 3. Micrographics corresponding to the addition of ammonium carbonate: (A) Distributions in spike form; (B) Hetrogeneous distribution.

Morphologically through scanning electron microscopy, it has been appreciated the presence of agglomerates of β-Si_3N_4 fibres together with other less numerous groups of α-Si_3N_4 particles. This distribution appeared in the experiments with addition of ammonium halides (NH_4F and NH_4Cl) and was quite constant along each sample (Fig. 2). However, with the rest of the salts the distributions and forms of the products are much more heterogeneous. In the case of incorporation of ammonium carbonate (exp. *SN 1.f* and *SN 2.f)* these forms are arbitrary and it has not been observed any orientation or preferential distribution (Fig. 3).

4. Conclusions

1. Additives in form of ammonium salts play a very important role in the combustion reaction, improving the access of nitrogen to raw materials mixture and favouring the nitridation process.
2. The incorporation of salts to the raw materials mixture affects to the presence of phases and its contents. Salts from organic acids produce oxynitrides and possibly silicon carbide formations, complicating the analysis of product data and their characterisation.
3. High percentages of α-Si_3N_4 are obtained with addition of NH_4Cl and ammonium carbonate. The disadvantageous generation of toxic gases is found when adding NH_4Cl. The existence of phases and complex morphologies is revealed when adding ammonium carbonate.

Acknowledgements

This work was supported by Spanish Science and Technology agency (CICYT) through the project MAT97-0728.

References

1. Ekelund, M. and Forslund, B., Carbothermal preparation of silicon nitride: influence of starting material and synthesis parameters. *J. Am. Ceram. Soc.*, 1992, **75**(3), 332–339.
2. Licko, T., Figusch, V. and Púchyová, Synthesis of silicon nitride by carbothermal reduction and nitriding of silica: control of kinetics and morphology. *J. Eur. Ceram. Soc.*, 1992, **9**, 219–230.
3. Janiga, J., Sin, K. P. and Figusch, V., Synthesis of silicon nitride powder by gas-phase reaction. *J. Eur. Ceram. Soc.*, 1991, **8**, 153–160.
4. Yamada, T., Preparation and evaluation of sinterable silicon nitride powder by imide decomposition method. *Am. Ceram. Soc. Bull*, 1993, **72**, 99–106.
5. Munir, Z. A. and Anselmi-Tamburini, U., Self-propagating exothermic reactions: the synthesis of high-temperature materials by combustion. *Mater Sci. Rep.*, 1989, **3**, 277–365.
6. Merzhanov, A. G. and Borovinskaya, I. P., A new class of combustion process. *Combust Sci. Technol.*, 1975, **10**, 195–201.
7. Merzhanov, A. G., Self-propagating high-temperature synthesis: twenty years of research and findings. In *Combustion and plasma synthesis of high-emperature materials*, ed. Z. A. Munir and J. B. Holt. VCH Publishers, New York, 1990, pp. 1–53.
8. Hlavacek, V., Combustion synthesis: a historical perspective. *Ceram. Bull.*, 1991, **70**(2), 240–243.
9. Hirao, K., Miyamoto, Y. and Koizumi, M., Synthesis of silicon nitride by a combustion reaction under high nitrogen pressure. *J. Am. Ceram. Soc.*, 1986, **4**, 60–62.
10. Hirao, K., Miyamoto, Y. and Koizumi, M., Combustion reaction characteristics in the nitration of silicon. *Adv. Ceram. Mater.*, 1987, **2**(4), 780–783.
11. Mukasyan, A. S., Martynenko, V. M., Merzhanov, A. G., Borovinskaya, I. P. and Blinar, M. Y., Mechanism and principles of silicon combustion in nitrogen. *Fiz. Gor. Vzryva*, 1998, **22**(5), 43–49.
12. Golubjatnikov, K. A., Stangle, G. C. and Spriggs, R. M., The economics of advanced self-propagating high-temperature synthesis materials fabrication. *Am. Ceram. Soc. Bull.*, 1993, **72**(12), 96–102.
13. Ge, C.C.., Li, J.T. and Xia, Y.-L. On the mechanism of self-propagating high-temperature synthesis (SHS) of Si_3N_4. *Int. J. SHS*, 1996, **5**(2).
14. Zhang, B.L., Zhuang, H.R. and X. R. Fu. A mechanism and tentative activation energy for the combustion reaction process of silicon in a pressurised nitrogen atmosphere. *J. Mater. Syn. Proc.*, 1997, **5**(5).

15. Hirao, K., Miyamoto, Y. and Koizumi, M., Combustion synthesis of nitride powders under high nitrogen pressure. *Adv. Ceram*, 1988, **21**, 289–300.
16. Li, J. T. and Ge, C. C., Investigation on the microstructural aspects of Si_3N_4 produced by self-propagating high-temperature synthesis. *J. Mater. Sci. Lett.*, 1996, **15**, 1051–1053.
17. Lee, W.-C. and Chung, S.-L., Combustion synthesis of si_3n_4 powder. *J. Mater. Res.*, 1997, **12**(3), 805–811.
18. Rodriguez, M. A. and Makhonim, N. S. et al., Single crystal β-Si_3N_4 fibers obtained by self-propagating high-temperature synthesis. *Adv Mater.*, 1995, **7**(8), 745–747.
19. Cao, Yeong-Ge., Ge, Chang-Chung, Zhou, Zhang-Jian and Li, Jiang-Tao Combustion synthesis of α- Si_3N_4 whiskers. *J. Mater. Res.*, 1999, **14**(3).
20. Liebig, Berthold and Puszynski, J. A., High pressure synthesis of silicon nitride-based materials with controlled morphology and phase composition. *Int. J. SHS*, 1998, **7**(1).
21. Rodríguez, M. A. et al., Single crystal β-sialon fibers obtained by self-propagating high-temperature synthesis. *Scripta Mater.*, 1997, **35**(4), 405–410.
22. Merzhanov, A.G., Borovinskaya, I.P., Popov, L.S., Makhonin, N.S., Kustova, L.V. Method of obtaining silicon nitride with high α phase content. WO Patent no. 89/11447, 1989.
23. Gazzara, C.P. and Messier, D.R.. Determination of phase content of Si_3N_4 by x-ray diffraction analysis. *Ceram. Bull.*, 1997, **56**(9).
24. Chung, S.L., Yu, W.L. and Lin, C.N. A self-propagating high-temperature synthesis method for synthesis of AlN powder. *J. Mater. Res.*, 1999, **14**(5).