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Effect of nitrogen pressure and oxygen-containing impurities on self-propagating high temperature synthesis of Si_3N_4

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Abstract

The effects of nitrogen pressure and oxygen-containing impurities on self-propagating high-temperature synthesis (SHS) of Si_3N_4 were studied. The growth mechanism of β-Si_3N_4 columnar crystal was investigated in detail using a gas-releasing method. The growth of α-Si_3N_4 occurred by a vapor-phase reaction, and the columnar β-Si_3N_4 grew by the vapor–liquid–solid (VLS) mechanism. Increase of the nitrogen pressure promoted volatilization of Si, and formation of α-Si_3N_4 during combustion, but did not favor the transition of the initial α-Si_3N_4 to β-Si_3N_4 during cooling. Therefore, the α/β ratio in the product increased with increasing nitrogen. Moisture in the nitrogen was helpful to the conversion of Si to α-Si_3N_4. Liquid formation, required by the VLS mechanism, depended upon the impurities containing oxygen in the reactant, rather than that in the nitrogen gas. The aspect ratio of columnar β-Si_3N_4 depended on the oxygen content in the reactant and the distribution coefficient of oxygen in the solid and liquid. Short β-Si_3N_4 columnar crystal was generally achieved because oxygen cannot get a supply from nitrogen gas. Increase of the oxygen content in the reactant resulted in a great improvement of the ratio of length and diameter of β-Si_3N_4. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Aspect ratio; SHS; Si; Si_3N_4; VLS

1. Introduction

Silicon nitride (Si_3N_4) as a high-temperature engineering ceramic attracted more attention because of its promising thermo-mechanical properties, such as high-temperature mechanical strength, durability, thermal shock resistance, chemical corrosion resistance, etc. A major application of silicon nitride ceramic aimed in the construction of a gas-turbine engine. If the target is realized, fuel savings of up to 40% for a given power output should be possible. In addition, the engine would be lighter and constructed from cheap and readily available materials.[1]

Self-propagating high-temperature synthesis (SHS) technology attracted the interest of many researchers as an energy and time-saving process.[2,3] Compared with Si_3N_4 powders prepared by other methods, SHS Si_3N_4 powders have a lower level of contamination, a higher degree of conversion, etc.

The growth mechanism of nitride in a combustion wave had been studied, yet no satisfactory explanation was obtained[4]. In order to reveal the growth mechanism of nitride prepared from elements (such as Si, Al, B and Ti, etc) and nitrogen by a combustion reaction, a new technology (a gas-releasing method) has been developed. The growth mechanism of AlN by SHS had been successfully investigated using this method.[5,6]

Effect of nitrogen pressure and the impurities containing oxygen on SHS of Si_3N_4 were studied in this paper. The growth mechanism of the β-Si_3N_4 columnar crystal was investigated in detail by a gas-releasing method.

2. Experimental procedure

Commercial available Si powders with a −100 mesh, and self-made Si_3N_4 powders by SHS with an average α/β ratio of about 76:23 as a dilute were used as the starting materials in this study. The silicon powders were ball-milled in a stainless-steel container for 24 h for using as a reactant. The content of oxygen and the main

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metallic impurity (Fe) in the ground silicon powders and initial Si_3N_4 powders were as follow: Si, O2 = 1.2 wt.%, Fe = 0.39 wt.%; and Si_3N_4, O2 = 0.5 wt.%, Fe = 0.22 wt.%. Their morphology is shown in Fig. 1. The composition of the mixtures and combustion condition is summarized in Table 1.

The mixture was mixed with twice weight of small Al_2O_3 balls in a plastic container for 24 h. After being vacuum-dried, the mixture was pressed into several cylinder compacts of approximately 30 mm in diameter and 60 mm in height, and wrapped with paper. Oxygen gas in the chamber was removed by means of pumping into and then out 5 atm N_2 twice. Then the chamber was back-filled with commercial available nitrogen, or high purity nitrogen (99.99%). The self-propagating reaction was initiated by igniting the pre-piled fine Ti powder on the top of the compact with a heating tungsten coil.

Combustion temperature was measured with a W-5% Re vs W-26% Re thermocouple, connected with a data-collecting system. The junction of thermocouple was placed in a hole of the sample, 20 mm far from the top. Morphology of the product was characterized by scanning electron microscopy (SEM). The elemental compositions in some micro-area are analyzed using X-ray energy dispersive spectroscopy (EDS). The content of α- and β-Si_3N_4 were semi-quantitatively analyzed according to the intensity of X-ray diffraction peaks.

In order to make clear the growth mechanism of Si_3N_4, a gas-releasing technology was developed. Most of the procedure of the gas-releasing experiments was similar with SHS experiments. Besides that, nitrogen gas was very rapidly released from the chamber in the gas-releasing experiments while combustion wave was proceeding along the sample. Because released nitrogen gas carried a large amount of heat away, afterburning was inhibited and combustion was quenched. We can induce what happened in SHS reaction on basis of the information that was protected from afterburning.

3. Results and discussion

3.1. The effect of nitrogen pressure

Combustion temperatures (the maximum temperature) of sample A1, A2 and A3 were approximately 1950, 2000 and 2100°C, respectively. It was obvious that

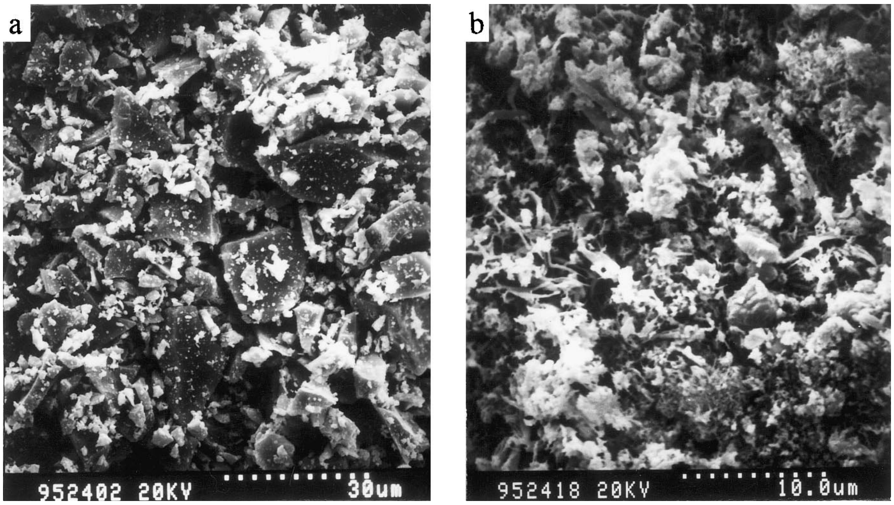


Fig. 1. Morphology of (a) the ground silicon and (b) the initial Si_3N_4 powders.

Table 1
Composition and combustion condition of samples

Sample no.	Si_3N_4 (%)	Si	SiO_2 (%)	Nitrogen pressure (MPa)	Commercial available nitrogen	Super-high purity nitrogen	The out-gas experiment
A1	50	50		3	√		
A2	50	50		5	√		
A3	50	50		10	√		
A4	50	50		10	√		√
A5	50	50		10		√	
A6	50	50		10		√	√
A7	40	50	10	10	√		

combustion temperatures slightly increased with increasing nitrogen pressure.

XRD patterns of combustion products at the nitrogen pressure of 3, 5 and 10 MPa are shown in Fig. 2a–c, respectively. Absence of silicon diffraction peak in Fig. 2 illustrated that full conversion of silicon to silicon nitride was achieved. The short hexagonal columnar crystal predominated in the samples A1, A2 and A3 as shown in Fig. 3. The crystal was generally considered as β-Si_3N_4.

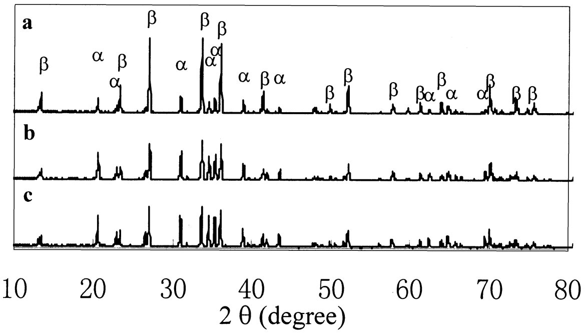


Fig. 2. X-ray diffraction patterns of the combusted product in the different samples: (a) A1, (b) A2, (c) A3.

According to the results of semi-quantitative analysis of the intensity of X-ray diffraction peaks, the ratios of α- to β- Si_3N_4 at the nitrogen pressure of 3, 5 and 10 MPa were 20:79, 29:70 and 43:56, respectively. The conversion ratio of Si to α-Si_3N_4 was promoted by increasing the nitrogen pressure. The α/β ratio was 76:23 in the initial Si_3N_4. If no α-Si_3N_4 in the dilute had transited into β-Si_3N_4 during combustion, the α- and β-Si_3N_4 ratio in the product should be approximately 30:70 while all silicon was converted to β-Si_3N_4. It means that some α-Si_3N_4 in the dilute was converted to β-Si_3N_4 during combustion.

It was generally believed that the growth of α-Si_3N_4 occurred by a vapor-phase reaction (a reaction between Si vapor and nitrogen)[1]. The increase of combustion

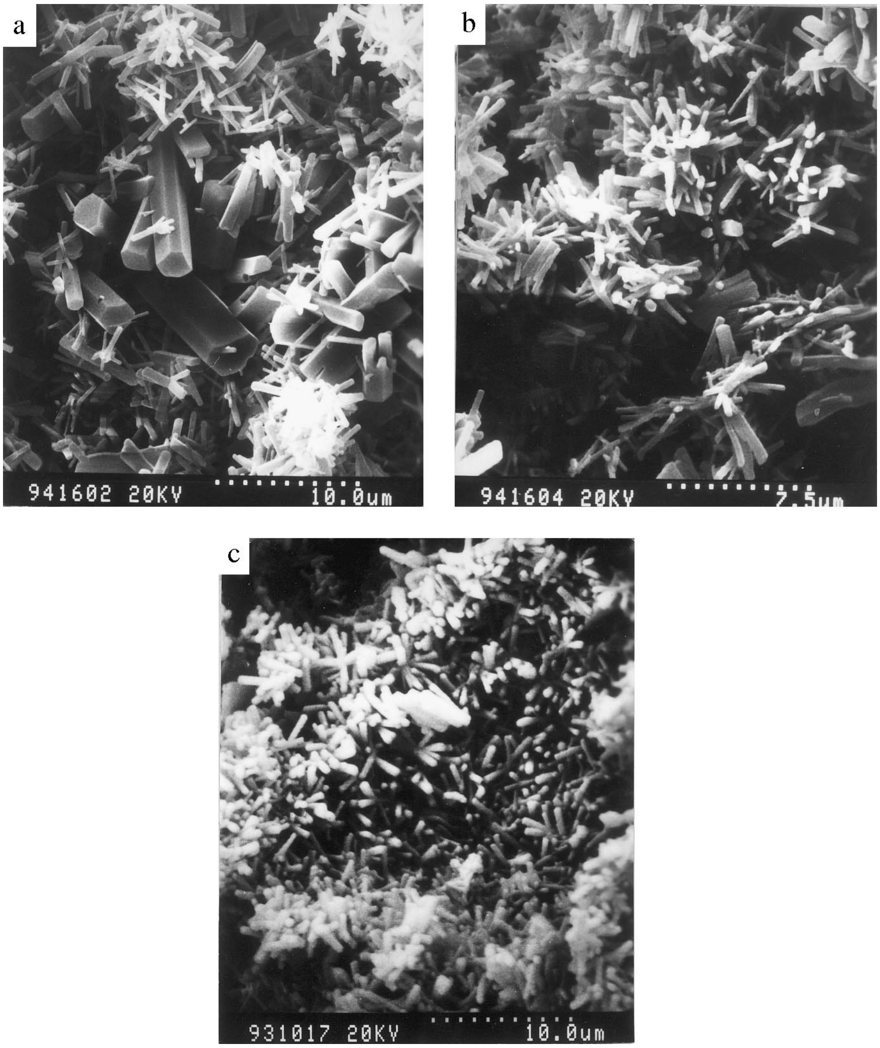


Fig. 3. Morphology of the combusted product in the different samples: (a) A1, (b) A2, (c) A3.

temperature promoted volatilization of Si, which favored the formation of α-Si_3N_4. Hence, the conversion ratio of Si to α-Si_3N_4 increased when increasing nitrogen pressure.

It was unavoidable that α-Si_3N_4 dilute was converted to β-Si_3N_4 during combustion. The α-β phase transition required a reconstruction of crystal lattice by a solution-reprecipitation or decomposition volatilization condensation (DVC) mechanism. It had been argued that the solution reprecipitation mechanism of the α-β phase transition was a predominant mechanism during combustion, especially in the stage of afterburning.[4] The higher nitrogen pressure was, the higher combustion temperature, what is more, the more the consumption of Si was in the combustion zone.[5] Therefore, the temperature and sustained time of afterburning increased, which favored the transition of the initial α-Si_3N_4 to β-Si_3N_4. It was one of important reasons that the α/β ratio in the combustion product under the lower nitrogen pressure was lower than that under the higher nitrogen pressure.

3.2. The effect of the impurities containing oxygen

XRD patterns of the combustion product under a pressure of 10 MPa of high purity nitrogen (99.99%) are shown in Fig. 4a. The α- and β-Si_3N_4 ratio in the combustion product under the high purity nitrogen was 21:78, lower than 43:56 under the commercial available nitrogen. It was reported that addition of H_2O in the nitrogen had affected the course of the reaction since not only was SiO generated but its nitridation was assisted by the parallel formation of H_2. An enhanced rate of formation of α-Si_3N_4 had been achieved.[1] In addition, α-Si_3N_4 needles can be developed by a vapor reaction involving the SiO molecule.[1] Moisture in the nitrogen was helpful to the improvement of the α/β ratio in the product. Therefore, The α/β ratio in the combustion product under the commercial available nitrogen was higher than that under the high purity nitrogen.

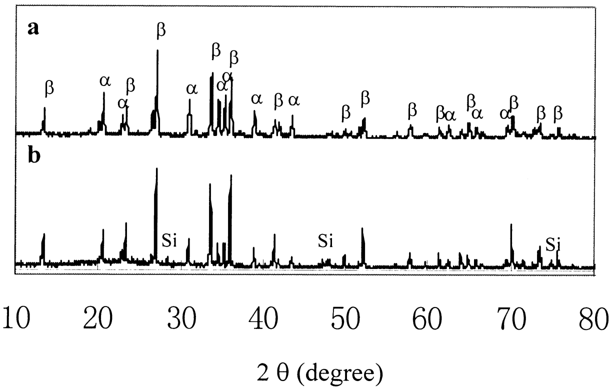


Fig. 4. X-ray diffraction patterns of the combusted product in (a) the sample A5 and (b) sample A7.

The combustion product in the sample A7 with 10 wt.% quartz powders consisted of α-Si_3N_4, β-Si_3N_4, and Si as shown in Fig. 4b. Despite of addition of quartz powders, no silica (or quartz) and Si–N–O ternary compound were found in the product.

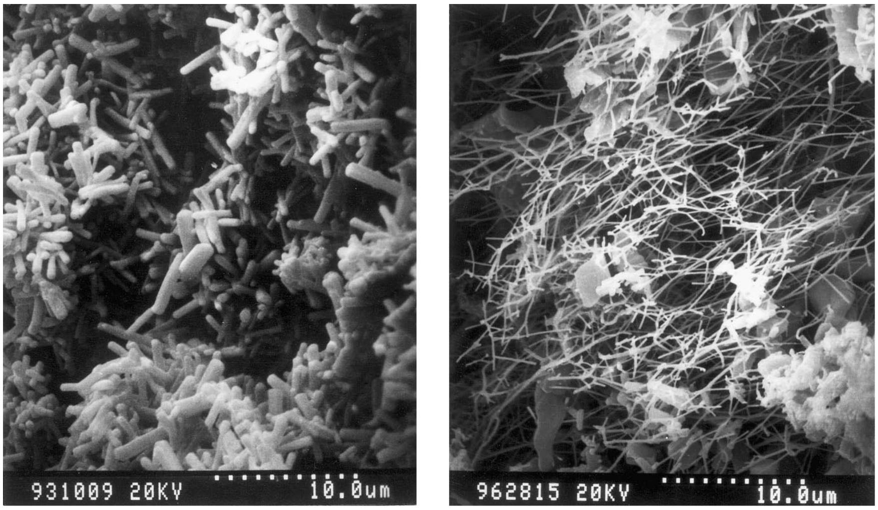
The short hexagonal columnar crystal predominated in the sample A5 as shown in Fig. 5a. A lot of fiberlike crystal presented in the sample A7 as shown in Fig. 5b, which illustrated that increase of the oxygen content in the reactant can greatly improve the aspect ratio of β-Si_3N_4.

3.3. The growth mechanism

An intermediate morphology of the growing β-Si_3N_4 in the gas-releasing samples (A4 and A6) is given in Fig. 6. Almost every columnar crystal had a round tip. The results of X-ray energy dispersive spectroscopy demonstrated that the droplets contained N, O, C and Si as shown in Fig. 7. The C mainly came from the sprayed one on the samples' surface for electricity conduction in convenience of observing under the microscope. The results strongly suggested that the columnar crystal grew by the vapor–liquid–solid (VLS) mechanism, which agreed with Mukasyan' results, the VLS mechanism should be considered as the most important growth mechanism of SHS of β-Si_3N_4.[4] Existence of oxygen at the tip of columnar crystal illustrated that the liquid formation required by the VLS mechanism may result from the impurities containing oxygen.

Though without moisture and oxygen in the high purity nitrogen, the growth of β-Si_3N_4 by the VLS mechanism was hardly affected. Moreover, the amount of the β-Si_3N_4 in the product was increasing. It was obvious that the oxygen, required by formation of liquid, should mainly come from the initial materials, rather than from nitrogen gas.

Oxygen should redistribute between β-Si_3N_4 and liquid while β-Si_3N_4 was growing by the VLS mechanism. Because it hardly got a supply from the nitrogen gas, the length of columnar β-Si_3N_4 crystal was determined by oxygen content in the reactant and the distribution coefficient of oxygen, $k = C_s/C_l$, where C_s and C_l are the solubilities of oxygen in the solid and liquid, respectively.[7] With the β-Si_3N_4 columnar crystal growing, the oxygen content in the liquid decreased. Hence, the short β-Si_3N_4 columnar crystal was generally achieved. It was somewhat different from the growth of combustion synthesized AlN whiskers by the same mechanism (VLS). The oxygen in the liquid at the tip of whiskers was continually supplied by the moisture in the nitrogen during combustion, therefore, AlN whiskers with high aspect ratio were generally obtained.[5,6]



(a) (b)

Fig. 5. Morphology of the combusted product (a) in the sample A5 and (b) sample A7.

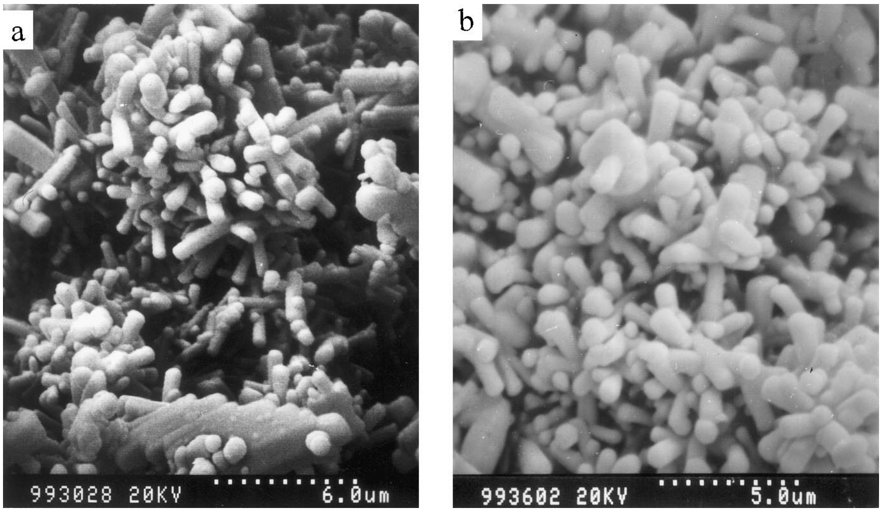


Fig. 6. Morphology of the combusted product in (a) the sample A4 and (b) sample A6.

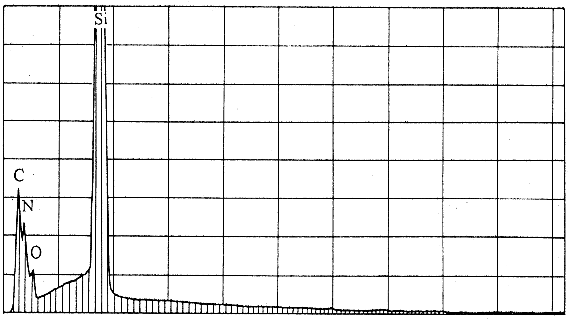


Fig. 7. X-ray energy dispersive pattern of the droplet at the tip of columnar crystal.

The presence of β-Si_3N_4 with higher aspect ratio presented in the sample A7 with 10 wt.% quartz powders further verified that the oxygen, required by formation of the liquid, mainly came from the raw materials, rather than from nitrogen gas.

4. Summary

The growth of α-Si_3N_4 occurred by a vapor-phase reaction, and the columnar β-Si_3N_4 grew by the VLS mechanism. Increasing nitrogen pressure promoted volatilization of Si, and formation of α-Si_3N_4 during combustion, but did not favor the transition of the initial α-Si_3N_4 to β-Si_3N_4 during afterburning. The α/β ratio in the product increased with increasing nitrogen pressure. Moisture in the nitrogen gas was helpful to improvement of the conversion ratio of Si to α-Si_3N_4. The formation of the liquid, required by the VLS mechanism, depended upon the impurities containing oxygen in the reactant, rather than in nitrogen. The aspect ratio of columnar Si_3N_4 crystal depended on the oxygen content in the reactant and the distribution coefficient of oxygen in the solid and liquid. Because oxygen in the liquid hardly got a supply from nitrogen, the short columnar β-Si_3N_4 was generally achieved. Increasing the oxygen content in the reactant improved the aspect ratio of β-Si_3N_4.

References

1. Moulson, A. J., Review: reaction-bonded silicon nitride: its formation properties. *J. Mater. Sci.*, 1979, **14**, 1017–1051.
2. Merzhanov, A. G., Self-propagating high-temperature synthesis: twenty years of search and findings [C]. In *Combustion Plasma Synthesis of High-temperature Materials*, ed. Z. A. Munir and J. B. Holt. VCH publisher, New York, 1990, pp. 1–53.
3. Wang, H., Han, J.-C. and Du, S., New progress in advance in application of SHS. Sinica. *J. Functional Mater*. (in Chinese), 1997, **28**, 115.
4. Skibsyka, M., Szuls, A., Mukasyan, A. S. and Rogachev, A. S., Microstructural peculiarities of silicon nitride formed by SHS under high nitrogen pressure. *Inter. J. SHS*, 1993, **2**(1), 39–47.
5. Wang, H. B., Han, J. C., Zheng, Y. T. and Du, S. Y., Effect of nitrogen pressure on afterburning of SHS AlN. *Chinese J. Mater. Res.*, 2000, **14**.
6. Wang, H. B., Han, J. C., Zheng, Y. T. and Du, S. Y., Effect of additives on SHS AlN. *J. Chinese Ceram. Soc.*, 2000, **28**(1), 15–19.
7. Levitt, A. P. *Whisker Technology*, Wiley-Interscience Inc., 1970