SILICON NITRIDE POWDER

SYNTHESIZED BY THERMAL PLASMA METHOD[①]

Liang Shuquan, Huang Baiyun, Zheng Ziqiao
Central South University of Technology, Changsha 410083
Szepvolgyi J
*Research Laboratory for Inorganic Chemistry of Hungarian Academy of Sciences,
H-1502, Budapest, Hungary*

ABSTRACT   Nanosized amorphous Si_3N_4 powders were prepared from the reaction between $SiCl_4$ and NH_3 in a RF plasma torch with a specific geometry. The experiments are aimed at studying the relationships between synthesis parameters and nitrogen content of the product, mass distributions of the product and the by-product. The main experimental parameters included plasma power, the mole ratio of the reactants. The powder was characterized in terms of the chemical composition analysis and morphology observation. The crystallization behaviors were also investigated.

Key words Si_3N_4 nanosized powder   thermal plasma method

1 INTRODUCTION

The use of Si_3N_4 as a structural ceramic requires high quality powders as starting materials so that the excellent thermomechanical properties and resistance to oxidation can be obtained. Compositional and microstructural homogeneity and minimization of defects in a near-fully-dense ceramic are facilitated by fine-particle size powders. The tentative powder requirements for Si_3N_4 powder are a total impurity content, excluding oxygen, of $< 0.1\%$; a low oxygen content of $< 2\%$, and a specific surface area near 10 $m^2 \cdot g^{-1}$.

In various synthesis methods for Si_3N_4, three typical chemical reactions were involved. They are 1) nitridation of silicon or silicides[1], 2) carbothermic reduction of SiO_2 in nitrogen atmosphere[2], and 3) conversion of silicon halides by ammonia either directly or *via* precursors such as $Si(NH_2)_2$[3]. Other gas phase synthesis techniques include the work of Prochazka Greskovich[4], who reacted SiH_4 with NH_3 at atomsphere to synthesize Si_3N_4, and the work of

Hggerty *et al*[5], who used a CO_2 laser as the heat source for the synthesis of silicon, silicon nitride powders. However, most of these methods could not completely meet the above important criteria for Si_3N_4 powder qualities. This led to a lot of in-house synthesis study, among which thermal plasma methods are very characteristic. Particularly, plasma methods are well suited to the use of gaseous starting materials from which high purity product can be produced because extremely high purity gases are available. The objective of this study is to examine the effects of the experimental parameters on chemical composition, mass distributions of the products and the by-product. In addition, the morphology observation and crystallization investigation were also made.

2 APPARATUS AND PROCEDURE

The experimental apparatus consisted of ridio-frequency (RF) induced plasma generator (27 MHz, 7.2 kW), a power supply system, a reactor chamber with two specific ring slits for the inlet of reactant gases, and collective cham-

bers, a reactant and supplementary gas supply system, a cooling system, and an exhauset system as shown in Fig. 1. The reactor, where the plasma was produced and the reactants reacted and most of the products were collected, consisted of two main components: an inducer coil and a plasma torch, which was a cylinder with an inside diameter about 3 cm and a length of about 100 cm with one uper set of injectors and one lower set of injectors. Each of them consisted of a set of small slots of 2 mm each which were distributed uniformly around the perimeter of the reactor. The upper injector was placed at a distance of about 100 mm from the bottom of the inducer coil. This specific arrangement made it possible to have a more uniform distribution of the reactants along the plasma flame tail region with an increased residence time in hot zone.

Fig. 1   Schematic diagram of the plasma CVD apparatus

For preparation of Si_3N_4, $SiCl_4$ with a purity of above 98% and NH_3 with a purity of above 99.96% were used as starting materials. Argon with high purity was used as plasma and sheath gas, and the carrier for $SiCl_4$. The $SiCl_4$ was introduced into the plasma tail from the upper injector where it underwent thermal decomposition, reacted with NH_3 which was introduced from lower injector.

The powders formed in different parts in the collective system were separately collected. They were marked T_1 powder collected at near the plasma flame tail region, T_2 powder obtained from the middle part of the collective system, T_3

powder gathered from the colder parts of the collective system. In order to determine the quantities of the by-products such as NH_4Cl, the powders were calcined for 1 h at 400 °C in flowing nitrogen atmosphere. The nitrogen content of the products were compositely determined by chemical analysis method. The phase compositions were detected by infrared (IR) spectroscopy experimental results. The crystallization of the powder was performed on a program controlled heating furnace. The morphology of the power was examined by TEM.

3   RESULTS AND DISCUSSION

3.1   Powder synthesis

The effects of plasma power (P) under the condition of $NH_3/SiCl_4 \approx 70$ on the nitrogen content, the powder mass collected, and the weight loss after calcined at 400 °C for 1 h of the T_1, T_2, T_3 powders are shown in Fig. 2(a), (b), (c). It can be found that the plasma power (P) had great influence on the product mass collected, by-product content and nitrigen content in the synthesized powder. The order for weight loss of different powders was $T_3 > T_2 > T_1$. The nitrogen content order for different powder was $T_1 > T_2 > T_3$. This means that T_1 powder contained much more silicon nitride and less by-products. These results can be explained from the temperature distribution in RF reactor as showed in Fig. 3, which was calculated by Njan[6] method at $P = 3$ kW. The temperature distribution showed that in the central part of the section of the torch 1, temperature was higher than 9 000 °C which was high enough to ionize $SiCl_4$ and NH_3. The ionized reactants reacted to form silicon nitride products and some other by-products at lower temperature in the proper outside layer of the plasma field. In Fig. 3, it can be seen that near the reactor wall the temperature was about 1 000 °C. Being properly charged, most of the silicon nitride particles were forced to the reactor wall near the plasma flame tail region and condensed there by the centrifugal force of the plasma, which could be discribed by

$$F = q(\boldsymbol{J} \times \boldsymbol{B}) \tag{1}$$

$$\boldsymbol{J} = q \cdot n \cdot \boldsymbol{V} \tag{2}$$

where $\boldsymbol{J}$, q, n, $\boldsymbol{V}$, $\boldsymbol{B}$ are respectively the current density, charge, number density, velocity for the charged silicon nitride particle and magnetic field strength of the plasma. However, in torch 1 the temperature was high enough to keep the by-product being in gaseous state. The by-products together with some non-charged silicon nitride particles came down to the low part of the collector and then condensed, where the temperature was lower than the condensed points of the by-products. In addition, the silicon nitride attached on torch 1 could be nitrided furthermore, this resulted that the torch 1 powder had much less weight loss and much higher nitrogen content when the power was in optimum. However, when the power was much too high, it would induced some negative effects, which led the quantites and nitrogen content decreased. One of the main negative effects was that the enforced plasma would etch the former condensed products. Another negative effect was that with the increase of power, the temperature in the outside layer was also increased, this would result in the decomposition of the products. There-

fore, for our experimental set-up, there was an optimum effective power. From Fig. 2 this optimum power was about 3.0 kW.

The effects of the reactant mole ratio on the powder mass collected, weight loss and nitrogen content were examined. The main results are that the mole ratio of the reactants had also great effects on the preparation of the powder. In the $NH_3/SiCl_4$ mole ratio range of 70～140, with the increase of the $NH_3/SiCl_4$ ratio, the mass powder collected in the torch 1 and 2 was decreased, and increased for that of torch 3. The weight loss was increased for three kinds of powder. This means that with the increase of $NH_3/SiCl_4$ mole ratio, the amount of the by-products was increased, especially for torch 3. However, the nitrogen contents of the torch 1, 2, 3 were not very sensitive to the ratio of $NH_3/SiCl_4$. Therefore, it would be better for $NH_3/SiCl_4$ ratio to be kept at 70 or 50.

3.2 Evaluation and crystallization of the powder

Fig. 4 and Fig. 5 are a TEM micrograph and a typical IR spectrum of T_1 powder prepared with $NH_3/SiCl_4$ ratio of 70 and at 3 kW supply

Fig. 2 The effect of the applied power on the T_1, T_2, T_3 powder nitrogen content, mass collected, and weight loss after being calcined at 400 ℃ for 1 h

Fig. 5   Typical IR spectrum of the
T_1 - Si_3N_4 powder

Fig. 3   The temperature distribution in the
experimental plasma reactor

power respectively, which show that the power was nanosized with a mean particle size of about 30 nm. In IR spectrum, there was a broad infrared absoption near 1 000 cm^{-1} due to Si-N banding and 3 200 cm^{-1} absorption due to N-H banding. In addition, there were a few of small absorption peaks presented around 600 cm^{-1}. These suggested that the main phase of the powder be amorphous, but with a small amount of crystal phase, which was resulted from the crystallization of the as-synthesized amorphous powder during the synthesis process in the out-layer of the product, the temperature may be high

enough to induce the powder crystallization.

Since the as-synthesized powder is ultrafine and amorphous, the green density of the compacted body formed by common forming technologies is low. Therefore, in order to make the powder apply to produce engineering ceramics, it is necessary to make this amorphous powder transfer to crystalline. The heat treatment condition for crystallization of the as-synthesized powder was summarized into Tabel 1. The IR patterns for heat treatment samples are shown in Fig. 6. From this figure it could be found that the crystallization took place at about 1 450 ℃. According to Luongo's[7] estimation method for α-Si_3N_4 content from IR experimental results, the α-Si_3N_4 phase fraction in crystalline phase could reach 90% when the powder was fired at 1 450 ℃ for 6h. Fig. 7(a) is the TEM micrograph of the crystallites, which shows that the crystallites had an equiaxed grain morphology with about 0.1 μm mean particle size. The diffraction pattern shown in Fig. 7(b) indicates that the amorphous powder crystallized completely. These characteristics could meet the requirements for Si_3N_4 powder to produce the advanced Si_3N_4 ceramics.

4   SUMMARY

A nanosized Si_3N_4 powder was synthesized by using the RF plasma method with NH_3 and $SiCl_4$ as starting materials. This powder was

Fig. 4   TEM morphology of T_1 - Si_3N_4 powder

amorphous, with about 30 nm mean particle size. The most important factors which influenced the characteristics of the products were applied power and reactant mole ratio. The applied power optimum was about 3. 0 kW. It would be better for the mole ratio of $NH_3/SiCl_4$ to be less than 70. The high quality and great amount powder was collected in torch 1 area. The nitrogen content was about 38%. The powder crystallization took place at 1 450 ℃. By using 1 450 ℃ heat treatment for 6 h, the powder crystallized to form fine-grain particles with mean particle size 0. 1 μm (100 nm). These could meet

Table 1   Heat treatment conditions for silicon nitride powder

| Identification | Description | Heat Treatment | | |
		Atmosphere	Temp / ℃	Time / min
SN-A	As-synthesized			
SN-B	SN-A$^+$	N$_2$	400	60
SN-C	SN-B$^+$	N$_2$	1 100	60
SN-D	SN-C$^+$	N$_2$	1 350	30
SN-E	SN-C$^+$	N$_2$	1 400	30
SN-F	SN-C$^+$	N$_2$	1 450	30

Fig. 7   Typical TEM morphology (a) and diffraction pattern (b) for crystallized Si$_3$N$_4$ sample

Si_3N_4 starting material requirements quite well for the preparation of the advanced Si_3N_4 engineering ceramics.

REFERENCES

1   Lumby R J. US 3 937 792, February, 1976.
2   Johnson R C. US 3 244 480, April 1960.
3   Jacobson H W. US 4 036 053, July 1977.
4   Prochazka S, Greskorich C. Amer Ceram Soc Bull, 1978, 57: 579.
5   Steinfeld J I. Laser-Induced Chemical Processes. New York: Plenum Press, 1981: 165.
6   Njan Z, Mostaghimi J, Boulos M. Int J Heat Mass Transfer, 1993, 36(16) : 3909.
7   Luongo J P. J Electrochem Soc, 1983, 130 (7): 1560.

Fig. 6   IR spectra for some heat treatment samples listed in Table 1

(Edited by Zhu Zhongguo)