

# PREPARATION OF NANOSIZED SILICON NITRIDE POWDERS BY AMMONO SOL-GEL PROCESSING<sup>①</sup>

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**ABSTRACT** Silicon nitride ( $\text{Si}_3\text{N}_4$ ) powders were synthesized with silica sol, urea and carbon black by ammono sol-gel processing. Urea was dissolved in water and mixed homogeneously with silica sol. Ammonolysis of the aqueous solution could form a precursor, which was then mixed with carbon black and nitrided at 1300~1600 °C under a flowing  $\text{N}_2$  atmosphere. The precursor and final powder were characterized by X-ray diffractometry, infrared spectroscopy and transmission electron microscopy. Results showed that  $\text{Si}_3\text{N}_4$  powders with a size of 50~80nm and a content of more than 37% nitrogen can be obtained from the precursor annealed at 1500 °C under a  $\text{N}_2$  flow of 3 L/min for 2 h. Effects of ammonolysis and synthesizing conditions on the final products were investigated.

**Key words** silicon nitride nanosized powder ammonolysis sol-gel

## 1 INTRODUCTION

Silicon nitride( $\text{Si}_3\text{N}_4$ ) is an attractive material for high temperature applications because of its high strength, good oxidation and thermal shock resistance. The increasing interest in  $\text{Si}_3\text{N}_4$  ceramics has led to a demand for high-quality, low-cost powders. A variety of synthesis techniques have been used and investigated, including direct nitridation<sup>[1]</sup>, conversion of silicon halides by ammonia either directly or via precursors such as  $\text{Si}(\text{NH})_2$ <sup>[2, 3]</sup>, chemical vapor deposition by laser and plasma synthesis<sup>[4, 5]</sup> and carbothermal reduction<sup>[6, 7]</sup>.

In a view of high performance and low cost, carbothermal nitridation process has advantages over others in purity, stability and sinterability. However, silica source and processing are important for the properties of final product. Most industrial  $\text{SiO}_2$  powders are so coarse that are hardly mixed well with carbon black, which surely exerts a harmful effect on the purity and particle size of  $\text{Si}_3\text{N}_4$  powder. In order to develop a suitable technique for mixing raw materials homoge-

neously and activating the precursor, in the present work, an ammono sol-gel processing was tried for the synthesis of  $\text{Si}_3\text{N}_4$  powder. The process presented here has features including: (a) maintaining most advantages of sol-gel process by using an aqueous solution of silica sol and urea; (b) ammonolysis of the aqueous solution resulting in an activated precursor and (c) available for producing high performance  $\text{Si}_3\text{N}_4$  powder at low cost.

## 2 EXPERIMENTAL

Urea was dissolved in water and mixed homogeneously with silica sol. The aqueous solution was slowly heated up to 80 °C, then bubbled by ammonia under continuous stirring until the solution became strongly viscous. After drying, a precursor had been prepared.

The precursor was resolved in alcohol and mixed with carbon black by ball milling in a plastic pot with agate balls. For comparison, silica sol was directly used instead of ammono precursor. 0~5% crystal seed of  $\text{Si}_3\text{N}_4$  was intro-

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duced in the mixing process. The mixture was gelled and dried up to 120 °C, then nitrided at temperatures from 1 300 to 1 600 °C under a flowing N<sub>2</sub> atmosphere. Residual carbon in synthesized powders was removed at 600 °C for 4 h in air.

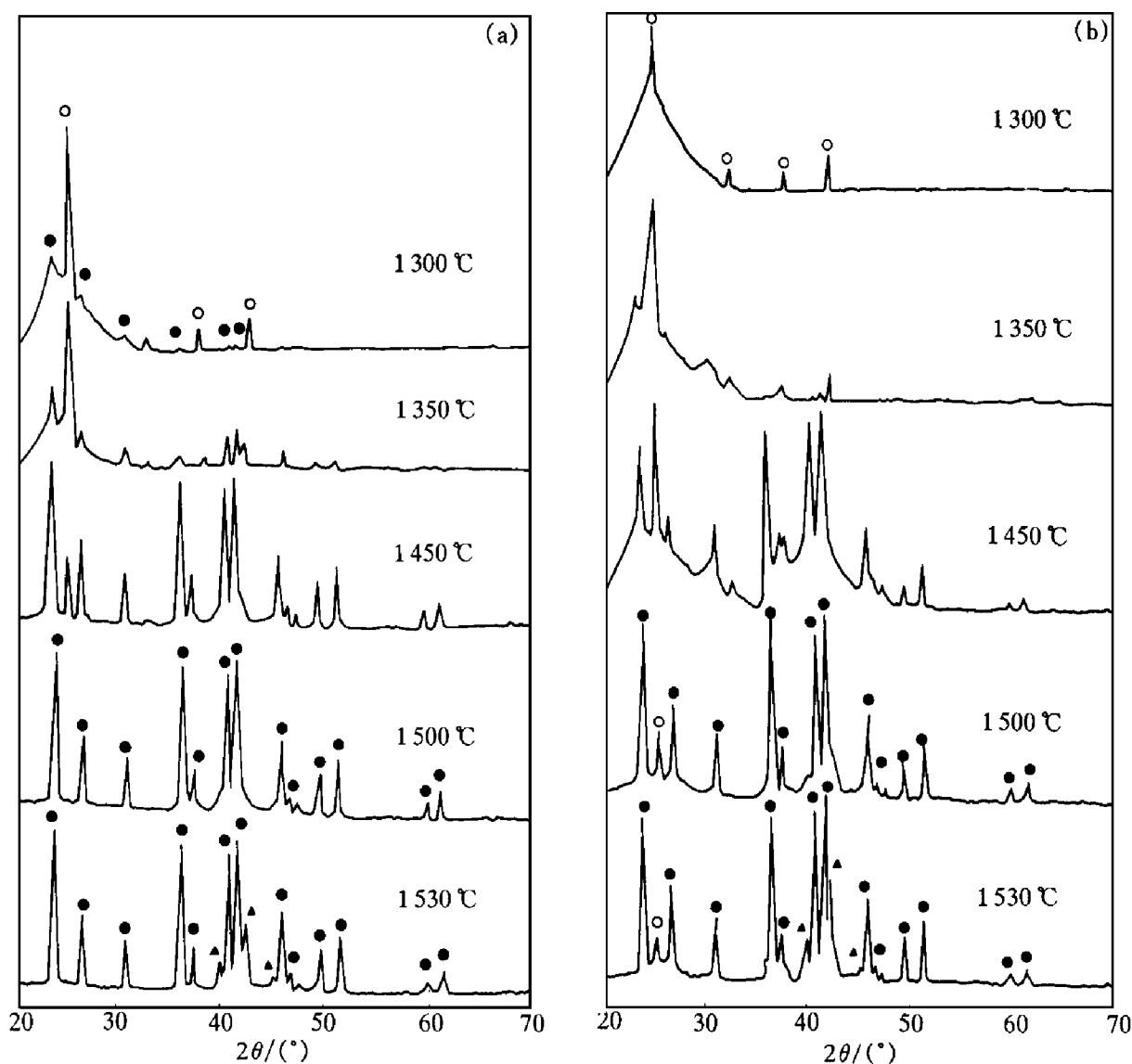
The final products were characterized by chemical analysis, X-ray diffractometry (XRD) and transmission electron microscopy (TEM). The precursor was investigated by infrared spectroscopy (IR).

### 3 RESULTS AND DISCUSSION

#### 3.1 Rule of Ammonolysis

XRD patterns of samples synthesized from ammono precursor and silica sol with a ratio of C/Si= 2.5 are shown in Fig. 1. For the ammono precursor system, Si<sub>3</sub>N<sub>4</sub> was detected at 1 300 °C and the intensity of Si<sub>3</sub>N<sub>4</sub> peaks increased with increasing temperature. At 1 500 °C, the carbothermal nitridation of SiO<sub>2</sub> completed and only Si<sub>3</sub>N<sub>4</sub> was observed. In silica sol system, Si<sub>3</sub>N<sub>4</sub> appeared at 1 350 °C, but the intensity was very weak. Silica and Si<sub>3</sub>N<sub>4</sub> phase coexisted between 1 350 and 1 500 °C. At 1 530 °C, SiC was detected and silica was still visual. Results illustrate that ammonolysis activated the reaction of carbothermal nitridation.

IR spectra of silica sol, urea and ammono



**Fig. 1 XRD patterns of powders at various temperatures**

(a) —From ammono precursor system; (b) —From silica sol system

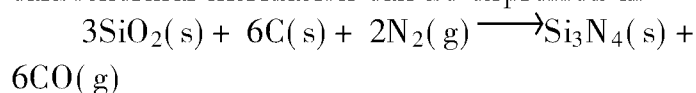
●—Si<sub>3</sub>N<sub>4</sub>; ○—SiO<sub>2</sub>; ▲—SiC

precursor are shown in Fig. 2. Ammonolysis of the aqueous solution of silica sol and urea resulted in dehydration of silica sol, which might prevent the formation of agglomerates and decrease the activation energy of nitridation reaction.

TEM micrographs of powders synthesized at 1 500 °C are shown in Fig. 3. The particle sizes of  $\text{Si}_3\text{N}_4$  from ammono precursor and silica sol were 50~ 80 nm and 100 nm respectively. The difference might be a result from the good reactivity and high scatter of the precursor.

### 3.2 Effect of synthesizing conditions

The overall reaction occurring during the carbothermal nitridation can be expressed as



The stoichiometric molar ratio of C/Si is 2: 1. In practice, the amount of carbon required should be greater than this. Fig. 4 shows the ef-

fect of the amount of carbon on the nitrogen content of  $\text{Si}_3\text{N}_4$  powder in the ammono precursor system. The nitrogen content of  $\text{Si}_3\text{N}_4$  did not obviously vary with the increase of C/Si molar ratio at 1 500 °C. However, it decreased with the increase of C/Si ratio at 1 530 °C. This illustrates that the excess carbon promoted the formation of SiC at higher temperatures.

Fig. 5 shows the effect of  $\text{N}_2$  flow on nitrogen content of final powder. The nitrogen content of  $\text{Si}_3\text{N}_4$  powder increased with the increase of  $\text{N}_2$  flow. XRD results revealed that silica did not completely disappear under a  $\text{N}_2$  flow of 1 L/min and 2 L/min even at 1 530 °C in the case of silica sol system. CO partial pressure increased with the decrease of  $\text{N}_2$  flow, which prevented the nitridation of the precursor. The content of nitrogen could not be steadily increased when the  $\text{N}_2$  flow was over 3 L/min, so the suitable  $\text{N}_2$  flow is 3 L/min.

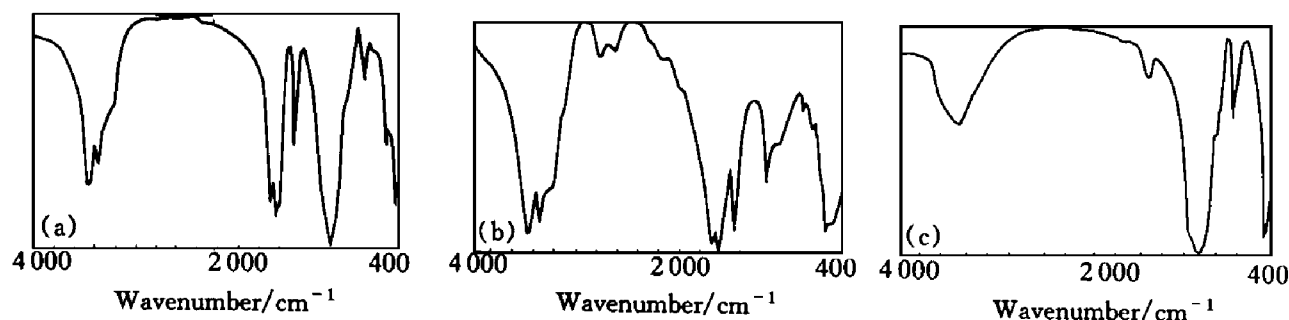


Fig. 2 Infrared spectra

(a) —Ammono precursor; (b) —Urea; (c) —Silica sol

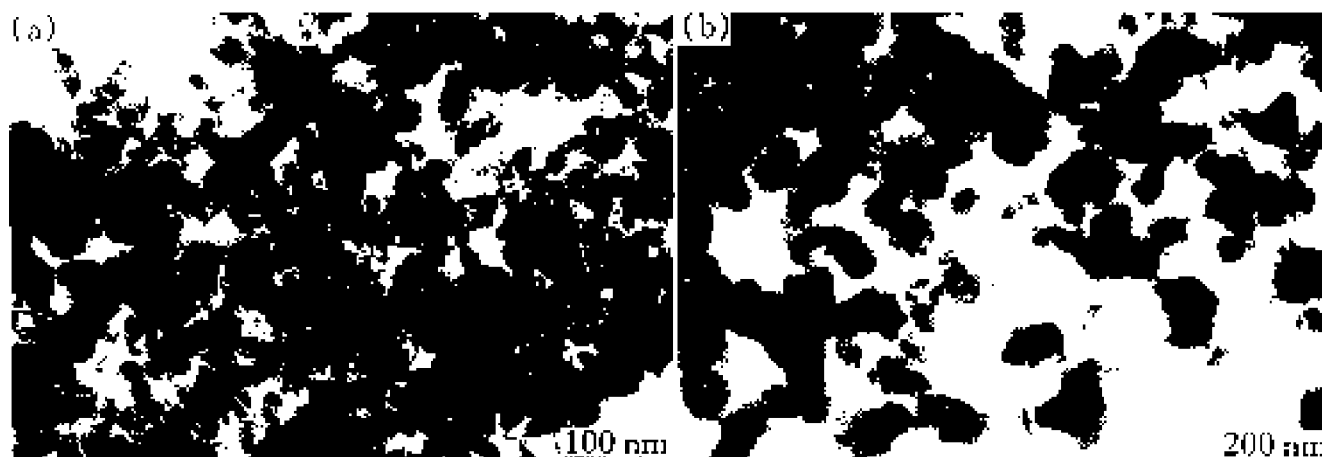


Fig. 3 TEM micrographs of  $\text{Si}_3\text{N}_4$  powders

(a) —From ammono precursor system; (b) —From silica sol system

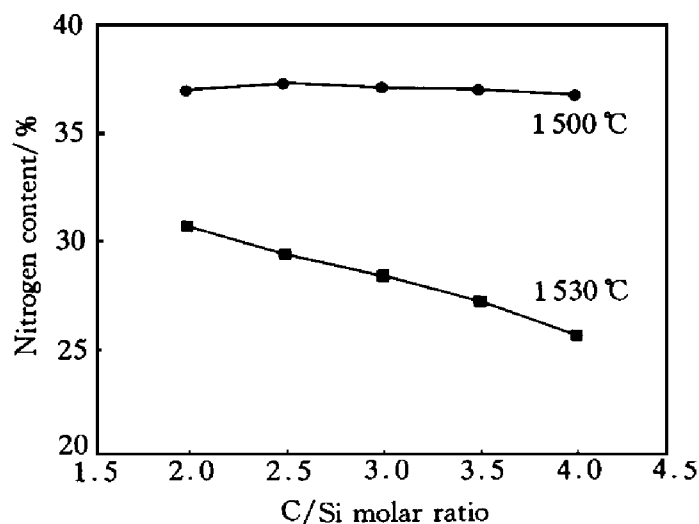


Fig. 4 Effect of C/Si molar ratio on nitrogen content of final products

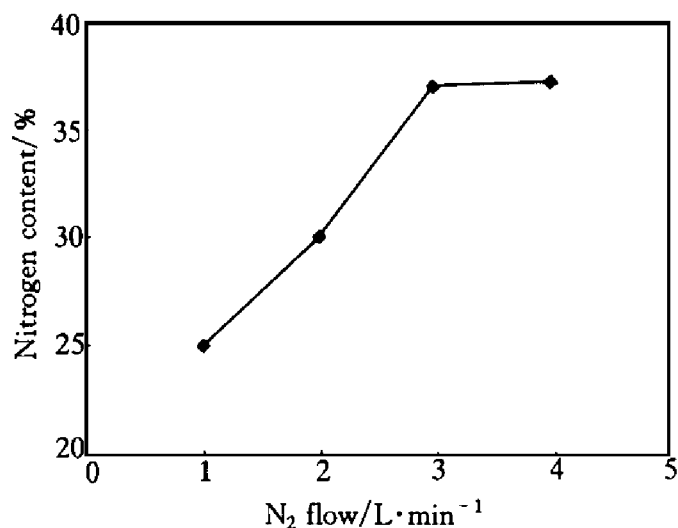


Fig. 5 Effect of N<sub>2</sub> flow on nitrogen content of final products

The effects of synthesizing temperature and time on nitrogen content of powders from the ammono precursor system are shown in Fig. 6 and Fig. 7. The nitrogen content of powders increased rapidly with the increase of temperature from 1450 to 1500 °C and reached a maximum (37.1%) at 1500 °C, then decreased above 1500 °C owing to the formation of SiC. The conversion from precursor to Si<sub>3</sub>N<sub>4</sub> can be finished in 1~2 h. The nitrogen content decreased slightly with the increase of synthesizing time because of the formation of SiC.

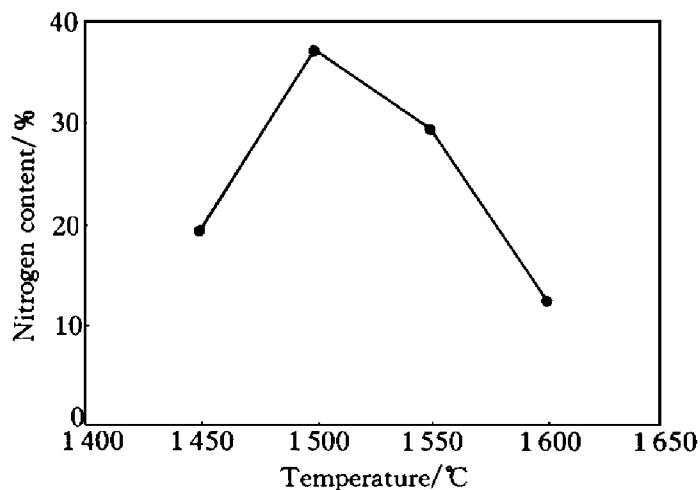


Fig. 6 Variation of nitridation temperature vs nitrogen content of products

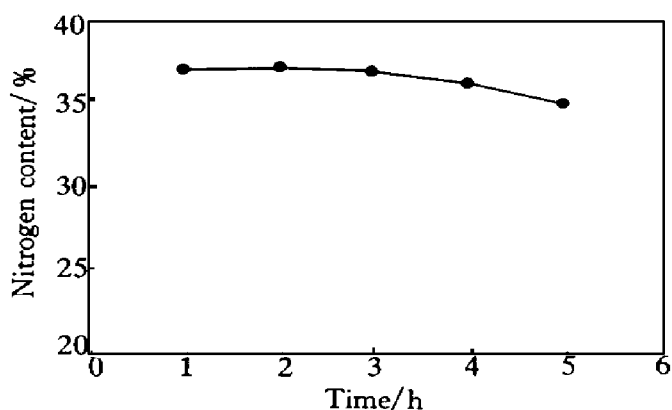


Fig. 7 Variation of nitridation time vs nitrogen content of products

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