

## Synthesis and crystallization of fine SiC-Si<sub>3</sub>N<sub>4</sub> composite powders by a vapor phase reaction

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In this study, ultra-fine SiC-Si<sub>3</sub>N<sub>4</sub> composite powders were synthesized by a vapor phase reaction using TMS (Tetra-methylsilane: Si(CH<sub>3</sub>)<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub> gases at reaction temperatures 1000~1200°C and with input ratios (NH<sub>3</sub>/Si(CH<sub>3</sub>)<sub>4</sub>) 1~3. XRD and TEM were used to analyze the crystalline phases and the average particle sizes of the synthesized composite powders. It was found that the powders obtained under the conditions chosen were all amorphous and spherical with a particle size of about 70~130 nm. The particle size was kept constant regardless of the input ratio, but it decreased with increasing reaction temperature. From the results of FT-IR and EA analysis, it was found that the synthesized powders had been formed from compounds composed of Si, N, C and H. After the synthesized composite powders of different input ratios were heat-treated for 2 hours at 1550°C in a N<sub>2</sub> atmosphere, crystalline β-SiC, α-Si<sub>3</sub>N<sub>4</sub> and β-Si<sub>3</sub>N<sub>4</sub> phases coexisted in the case of a low input ratio, while only the crystalline α-Si<sub>3</sub>N<sub>4</sub> phase appeared in the case of a high input ratio.

**Key words:** Ultra-fine composite, α-SiC, β-Si<sub>3</sub>N<sub>4</sub>, α-Si<sub>3</sub>N<sub>4</sub>, Chemical Vapor Deposition (CVD).

### Introduction

Silicon nitride (Si<sub>3</sub>N<sub>4</sub>) and silicon carbide (SiC) have many excellent properties such as high thermal strength, high corrosion resistance, high thermal shock resistance, high creep resistance and thermal conductivity, and low thermal expansion coefficient [1-6]. Thus silicon nitride and silicon carbide composite plays an important role as a high temperature structural material. However, Si<sub>3</sub>N<sub>4</sub> is very difficult to sinter because of the volatility and small diffusivity of Si and N. Hence, many studies are under way, mainly concerned with the synthesis of fine powders with high sinterability and there are several methods to produced fine Si<sub>3</sub>N<sub>4</sub> powder [7-11]. Among others a vapor phase reaction method has been widely used to synthesize nano-sized SiC-Si<sub>3</sub>N<sub>4</sub> composite powders [12]. Hence, in this study, we synthesized silicon nitride and silicon carbide nano-sized composite powders by a vapor phase reaction method to prevent the contamination created by a mechanical mixing method and to obtain the better properties [13-14]. The synthesized powders have been characterized and the crystallization behaviors was studied.

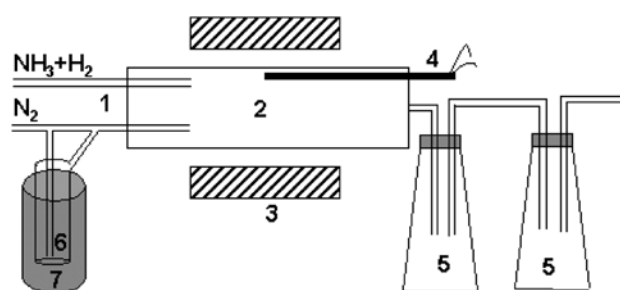
### Experiment Procedures

#### Powder synthesis

TMS [Tetramethylsilan: Si(CH<sub>3</sub>)<sub>4</sub>], ammonia (NH<sub>3</sub>, 99.999%) and hydrogen (H<sub>2</sub>, 99.999%) were used as reactants for the synthesis of silicon nitride and silicon carbide composite powders by a vapor phase reaction method. Figure 1 shows that the vapor phase synthesis apparatus consists of parts such as the reactor, a controller of the gas flow of TMS and NH<sub>3</sub> and the powder collection system. TMS was carried by N<sub>2</sub> from a bubbler into the reactor tube, where it was mixed with an NH<sub>3</sub>-H<sub>2</sub> mixture. The reaction conditions were as follows: (1) Reaction temperature: 1000~1200°C (2) input ratio (NH<sub>3</sub>/Si[CH<sub>3</sub>]<sub>4</sub>): 1~3 (3) total flow rate: 700 cc/minute (4) reaction time: 2 hr

Later the synthesized powders were heat treated at 1550°C for 2 hour in a nitrogen atmosphere.

#### Powder characterization techniques



1. alumina tube : LD - 4mm.300L
2. alumina tube : LD - 23mm. 1000L
3. furnace
4. R-type thermocouple
5. collecting flask
6. evaporator of (CH<sub>3</sub>)<sub>4</sub>Si
7. Ice box

Fig. 1. Reaction apparatus.

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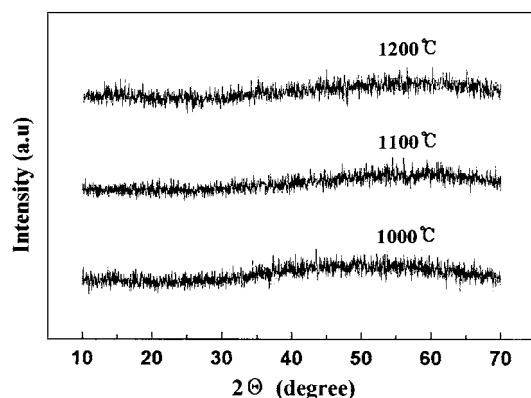
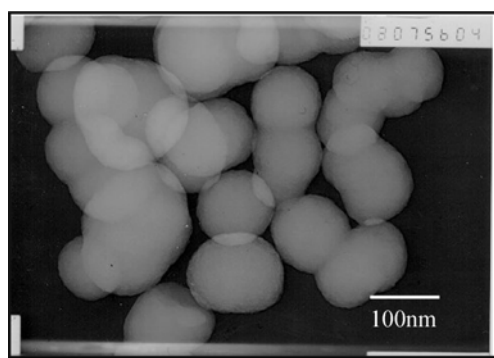
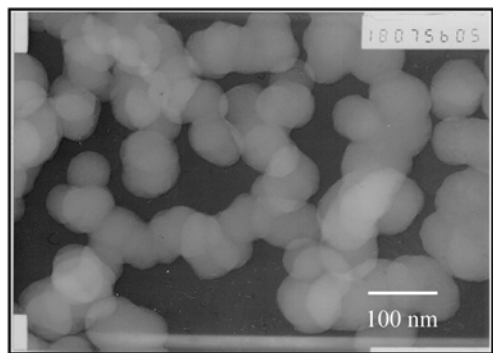


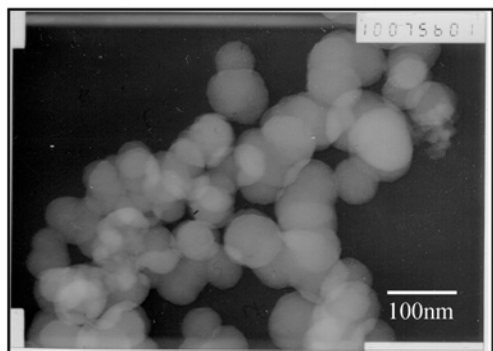
Fig. 2. X-ray diffraction patterns of synthesized powders as a function of reaction temperature. ( $\text{NH}_3/\text{Si}(\text{CH}_3)_4=1$ , total gas flow: 700 cc/minute)



(a) reaction temperature : 1000°C



(b) reaction temperature : 1100°C



(c) reaction temperature : 1200°C

Fig. 3. TEM photomicrograph of synthesized powders as a function of reaction temperature. ( $\text{NH}_3/\text{Si}(\text{CH}_3)_4=1$ , total gas flow: 700 cc/minute)

The synthesized composite powders were analyzed for the following properties: (1) the particle size and morphology, (2) the crystallinity (3) the silicon, nitrogen and carbon content, (4) the type of chemical bonding. The sizes and morphology of particles were determined by TEM. The powder crystallinity was analyzed by X-ray diffraction. Elemental analysis was used to measure the hydrogen, nitrogen and silicon content of the powders. The chemical bonding of the synthesized powders was measured by FT-IR transmission spectra using a KBr tablet method.

## Discussion and Result

### Effect of the reaction temperatures

The reaction temperature was varied from 1000°C to 1200°C whilst the total flow rate and input ratio was 700 cc/minute and 1, respectively. Figure 2 shows the X-ray diffraction output from the SiC-Si<sub>3</sub>N<sub>4</sub> composite powder as a function of reaction the temperatures. The synthesized powder formed was an amorphous over all this temperature range condition. Figure 3 shows the TEM microphotographs of the SiC-Si<sub>3</sub>N<sub>4</sub> powders. The powders were relatively uniform spherical particles with a particle size from about 70~130 nm. When the reaction temperature was increased, the particle size was decreased. Figure 4 shown, the stretching vibration of the Si-N bond, Si-C bond, Si-H bond, and N-H bond. Thus, it was established that the synthesized powder consisted of Si, N, C and H.

### Effect of the input ratio

The input ratio was changed from 1 to 3 and the total flow rate and reaction temperature was 700 cc/minute and 1200°C, respectively. Figure 5 shows X-ray diffraction pattern of the SiC-Si<sub>3</sub>N<sub>4</sub> composite powder as a temperature of the input ratio. This figure shown that the powders synthesized were amorphous at all input ratios. Also, in the TEM microphotographs shown in

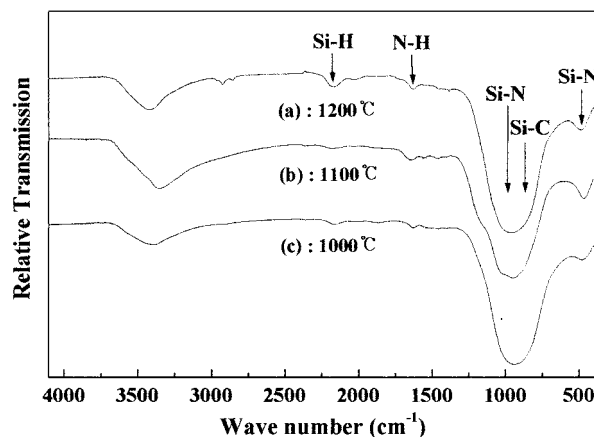
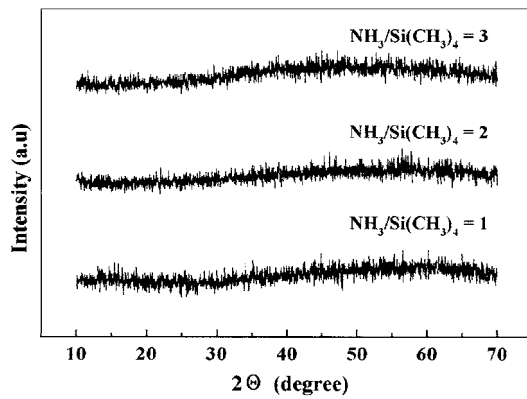
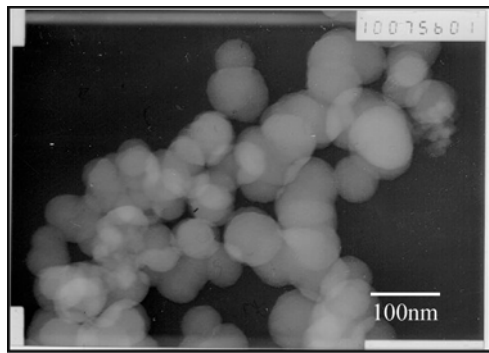


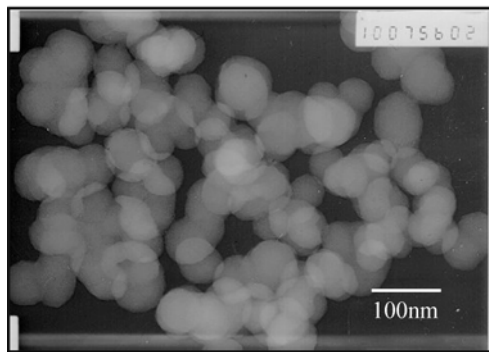
Fig. 4. FT-IR transmission spectra of synthesized powders as a function of reaction temperature. ( $\text{NH}_3/\text{Si}(\text{CH}_3)_4=1$ , total gas flow: 700 cc/minute)



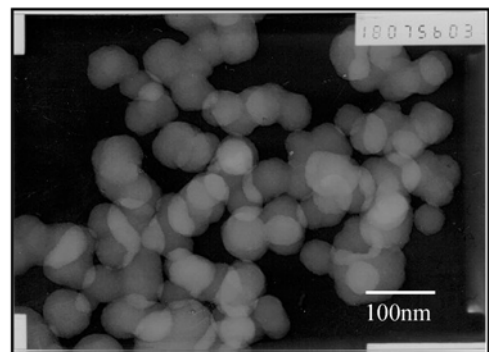
**Fig. 5.** X-ray diffraction patterns of synthesized powders as a function of the  $\text{NH}_3/\text{Si}(\text{CH}_3)_4$  ratio. (reaction temperature:  $1200^\circ\text{C}$ , total gas flow: 700 cc/minute)



(a)  $\text{NH}_3/\text{Si}(\text{CH}_3)_4 = 1$

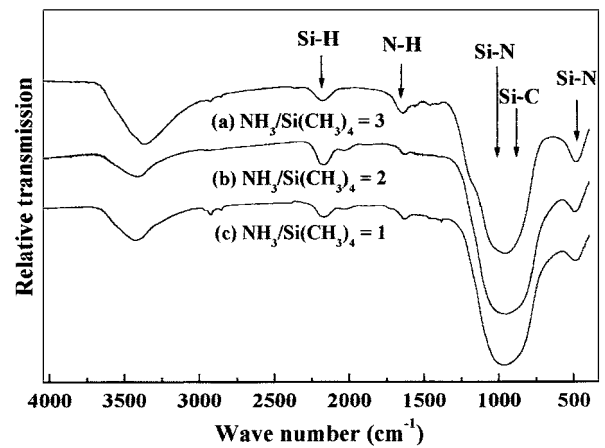


(b)  $\text{NH}_3/\text{Si}(\text{CH}_3)_4 = 2$



(c)  $\text{NH}_3/\text{Si}(\text{CH}_3)_4 = 3$

**Fig. 6.** TEM photomicrographs of synthesized powders as a function of the  $\text{NH}_3/\text{Si}(\text{CH}_3)_4$  ratio. (reaction temperature:  $1200^\circ\text{C}$ , total gas flow: 700 cc/minute)

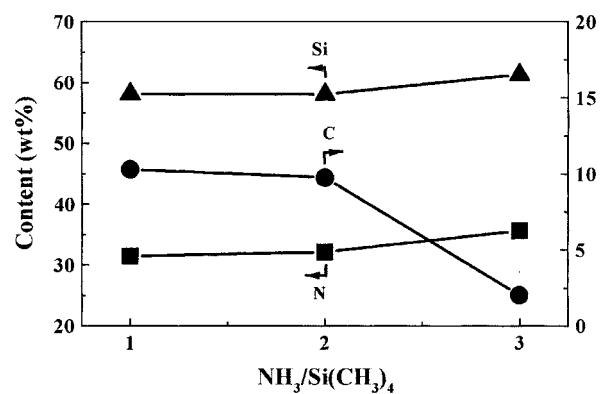


**Fig. 7.** FT-IR transmission spectra of synthesized powders as a function of the  $\text{NH}_3/\text{Si}(\text{CH}_3)_4$  ratio. (reaction temperature:  $1200^\circ\text{C}$ , total gas flow: 700 cc/minute)

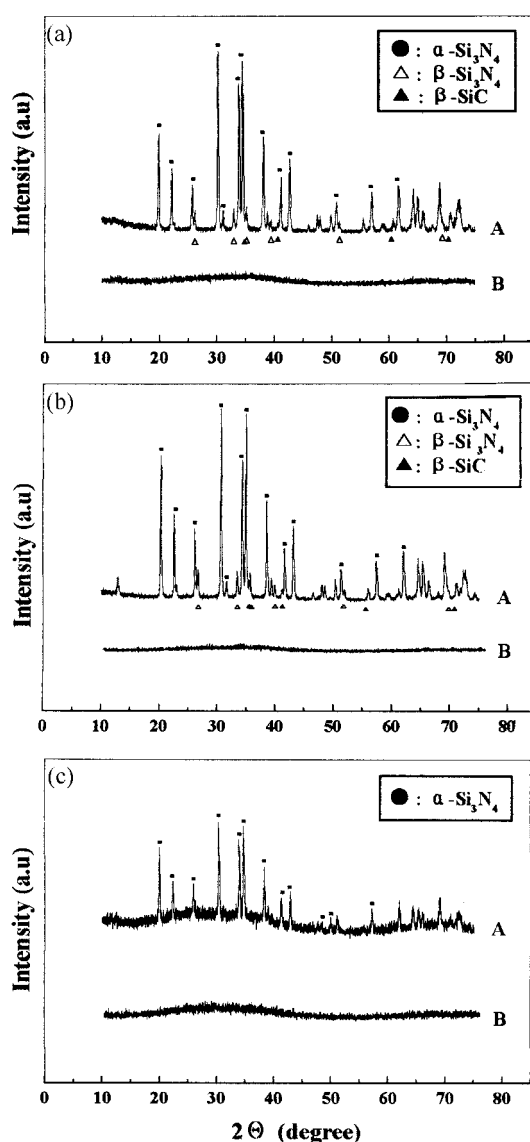
Figure 6, the particle shape was relatively spherical and particle size was about 70–80 nm. In spite of a change in the  $\text{NH}_3$  concentration, the particle size was almost constant. Figure 7 shows FT-IR transmission spectra from powders synthesized at various input ratios. The stretching vibrations of the Si-N bond, Si-C bond, N-H bond, and Si-bond are shown. When the  $\text{NH}_3$  concentration was increased, the stretching vibration of Si-N bond and N-H bond both increased. As shown in figure 8, the results of EA analysis, show that the synthesized composite powder was consisted Si, N, C, and H. When the input ratio was low, the carbon content was high but it sharply decreased when the input ratio was high. So, the synthesized powder from the high input ratio was the silicon nitride only.

### Crystallization

The synthesized powders were heat treated at  $1550^\circ\text{C}$  for 2 hour in a nitrogen atmosphere and the crystallinity was determined by the X-ray diffraction the patterns of which are shown Figure 9. As shown in this figure, crystalline  $\beta\text{-SiC}$ ,  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$  phases co-existed in the case of a low input ratio, while only



**Fig. 8.** Content of synthesized powders as a function of the  $\text{NH}_3/\text{Si}(\text{CH}_3)_4$  ratio.



**Fig. 9.** X-ray diffraction patterns of synthesized powders as a function of  $\text{NH}_3/\text{Si}_3\text{N}_4$  ratio after crystallization. (Heat treatment temperature:  $1550^\circ\text{C}$ , Time: 2 Hr, (a)  $\text{NH}_3/\text{Si}(\text{CH}_3)_4=1$ , (b)  $\text{NH}_3/\text{Si}(\text{CH}_3)_4=2$ , (c)  $\text{NH}_3/\text{Si}(\text{CH}_3)_4=3$ )

the crystalline  $\alpha\text{-Si}_3\text{N}_4$  phase appeared in the case of the high input ratio.

## Conclusions

SiC-Si<sub>3</sub>N<sub>4</sub> composite powders were synthesized by a chemical vapor phase reaction as a function of the reaction temperature and input ratio. From these experimental results, the following conclusions can be deduced:

(a) The synthesized powders were a spherical amorphous composite powders for all the experimental conditions and the powder size was about 70~130 nm. The particle size was independent of the variation of  $\text{NH}_3$  concentration, but decreased by increasing the reaction temperature.

(b) The heat treated synthesized composite powders showed different crystallization behavior by changing the input ratio. When the input ratio was low, the powders produced were SiC-Si<sub>3</sub>N<sub>4</sub> composite powders, but, when the input ratio was high, the powders produced were Si<sub>3</sub>N<sub>4</sub> only.

(c) The crystallinity was sharply decreased by increasing the  $\text{NH}_3$  concentration.

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