

# Liquid Phase Synthesis of Si<sub>3</sub>N<sub>4</sub>-TiN Composite Particle by Imide Method

Masato Uehara, Naoya Enomoto and Junichi Hojo

Department of Applied Chemistry, Faculty of Engineering, Kyushu University

6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-8581 Japan

Si<sub>3</sub>N<sub>4</sub> particle and Si<sub>3</sub>N<sub>4</sub>-TiN composite particle were prepared by liquid phase synthesis. The prepared particles had a imide structure. The microstructure evolutions of these particles by heat-treatment were investigated by IR, XRD, XPS and TEM. In Si<sub>3</sub>N<sub>4</sub> monolithic particle, IR analysis indicated a gradual transition from Si-imide to Si<sub>3</sub>N<sub>4</sub> occurring with elevating temperature. In Si<sub>3</sub>N<sub>4</sub>-TiN composite particle, TiN inclusions accelerated the crystallization of Si<sub>3</sub>N<sub>4</sub>. XPS and TEM analysis suggested that Ti-imide segregated on Si-imide surface and TiN was embedded in Si<sub>3</sub>N<sub>4</sub> particles during decomposition of imide particles.

Key words : silicon nitride, composite particle, liquid phase synthesis, imide, crystallization

## 1. INTRODUCTION

It has been well known that the function of ceramic composite has been improved significantly by control in nano-meter level [1]. It is difficult to finely and homogeneously disperse the second phase particles by a mechanical mixing process. Composite powders are very useful to control fine composite structure because each particle in composite powder has several components. Hojo has studied on the preparation of composite powders by a vapor phase method and their application for fabricating the nanocomposites [2,3]. In Si<sub>3</sub>N<sub>4</sub>-TiN composite powder, TiN inclusions under 10nm was finely dispersed in Si<sub>3</sub>N<sub>4</sub> particles. The nanocomposite fabricated from this composite powder exhibited an improved fracture toughness[4].

Fine Si<sub>3</sub>N<sub>4</sub> powder has been commercially produced by an imide decomposition process. Si(NH)<sub>2</sub> powder has been prepared by the reaction of SiCl<sub>4</sub> with NH<sub>3</sub> in the liquid phase and crystallized to Si<sub>3</sub>N<sub>4</sub> powder by heating [5]. If TiCl<sub>4</sub> is added to this process, the complex imide of Si-Ti-N-H system can be obtained and decomposed to Si<sub>3</sub>N<sub>4</sub>-TiN composite powder by heat treatment. In the present paper, Si<sub>3</sub>N<sub>4</sub>-TiN composite powder was prepared by a liquid phase reaction and imide decomposition. The structure and the phase separation behavior of the prepared composite particles during heating were investigated.

## 2. EXPERIMENTAL PROCEDURES

The Si<sub>3</sub>N<sub>4</sub>-TiN composite powder was synthesized as follows. SiCl<sub>4</sub> and TiCl<sub>4</sub> were dissolved into *n*-hexane in N<sub>2</sub> atmosphere. The solution was reacted with NH<sub>3</sub> gas at 0 or -20°C. The precipitate was heated at 400°C for 2h in vacuum to eliminate NH<sub>4</sub>Cl. After calcination at 900°C, the powder was further heat-treated at

1400-1500°C for 2h in N<sub>2</sub> for crystallization. For comparison, monolithic Si<sub>3</sub>N<sub>4</sub> powder was synthesized from SiCl<sub>4</sub> solution by the same method.

The crystalline phases were identified by XRD. The state of chemical bonding was evaluated by IR spectroscopy. The elemental distribution on the particle surface was analyzed by XPS. The particle morphology was observed by TEM. TiN contents of all composite powders were about 5vol%, determined by X-ray fluorescence (XRF) analysis.

The sintered bodies were fabricated by hot pressing, in which Y<sub>2</sub>O<sub>3</sub>(6wt%)-Al<sub>2</sub>O<sub>3</sub>(2wt%) sintering aid was used. The hot pressing was carried out for 2h at 1800°C in N<sub>2</sub>. The sintered density was measured by the Archimedes method. The microstructures of sintered bodies were observed by SEM.

## 3. RESULTS AND DISCUSSION

Figure 1 was the XRD patterns of as-precipitate and heated materials. The product synthesized from SiCl<sub>4</sub> solution at 0°C, was crystallized to α-Si<sub>3</sub>N<sub>4</sub> at 1500°C. In the case of SiCl<sub>4</sub>-TiCl<sub>4</sub> solution, TiN was already crystallized after 900°C calcination. The crystallization of α-Si<sub>3</sub>N<sub>4</sub> was accelerated and observed at 1400°C.

On the other hand, the peaks of α-Si<sub>3</sub>N<sub>4</sub> were weaker in products synthesized at -20°C than those of 0°C even after 1500°C heating.

Figure 2 shows the IR spectra of products synthesized from SiCl<sub>4</sub>-TiCl<sub>4</sub> solution at 0°C. The presence of Ti-N bond was not detected. The as-precipitated powder exhibited the peaks of Si(NH)<sub>2</sub> in addition to NH<sub>4</sub>Cl. The SiN-H stretching peak, and SiN-H<sub>2</sub> and SiN-H bending peaks were observed below 900°C. Above 1400°C, the peak of Si-N stretching mode became strong, indicating the change of an imide compound to Si<sub>3</sub>N<sub>4</sub>.

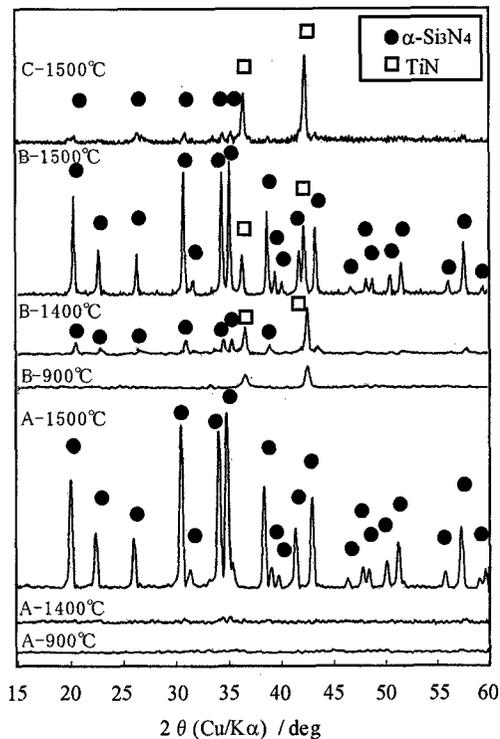


Fig.1 XRD patterns of powders. (A) monolithic  $\text{Si}_3\text{N}_4$  synthesized at  $0^\circ\text{C}$ , (B)  $\text{Si}_3\text{N}_4$ -TiN synthesized at  $0^\circ\text{C}$  and (C)  $\text{Si}_3\text{N}_4$ -TiN synthesized at  $-20^\circ\text{C}$ .

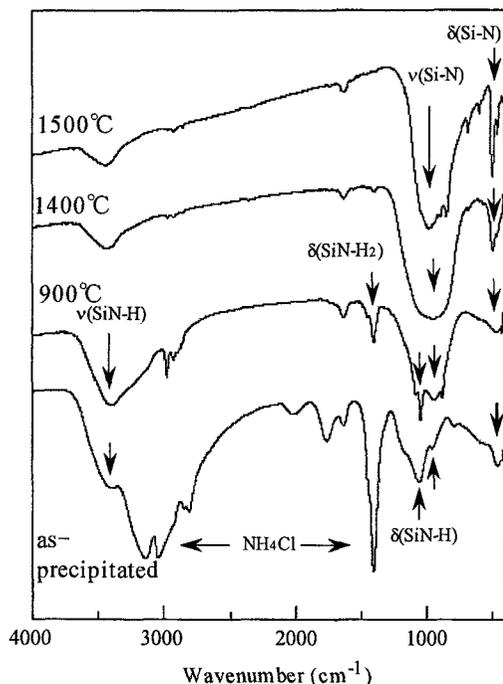


Fig.2 IR spectra of  $\text{Si}_3\text{N}_4$ -TiN composite powders synthesized at  $0^\circ\text{C}$ .

The elemental distribution on the surface of particles was analyzed by XPS. Figure 3 shows the peaks of  $\text{Si}_3\text{N}_4$ -TiN composite powders synthesized at  $0^\circ\text{C}$ . The N1s peak was shifted to lower binding energy by heat-treatment. This suggested the structure change from imide to  $\text{Si}_3\text{N}_4$ . The Si2p peak was weak in as-precipitated but became strong after heat-treatment. The Ti2p peak was observed in as-precipitated but disappeared after heat treatment.

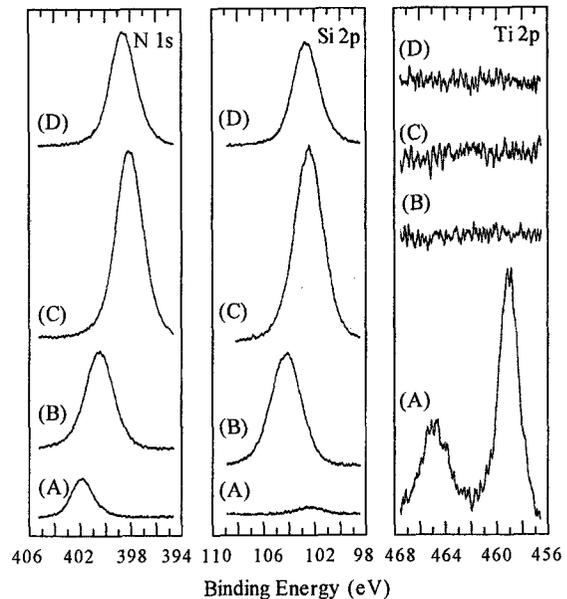


Fig.3 XPS peaks of  $\text{Si}_3\text{N}_4$ -TiN composite powders synthesized at  $0^\circ\text{C}$ . (A) as-precipitated, (B)  $900^\circ\text{C}$ , (C)  $1400^\circ\text{C}$  and (D)  $1500^\circ\text{C}$ .

Figure 4 shows TEM images of  $\text{Si}_3\text{N}_4$ -TiN composite powders synthesized at  $0^\circ\text{C}$ . The as-precipitated were agglomerated particles and 200-300nm in diameter. These were amorphous. According to TEM-EDX analysis, the X-ray intensity ratio of Ti to Si was increased, as closer on the surface. After heat-treatment at  $1500^\circ\text{C}$ , the particles crystallized to  $\text{Si}_3\text{N}_4$  and became square. TiN inclusions which size was 10-20nm were observed in  $\text{Si}_3\text{N}_4$  particles. These results of TEM and XPS analysis might suggest that Ti-imide segregated on the surface of Si-imide particles and, during the decomposition of imides to nitrides by heating, TiN particles were surrounded by  $\text{Si}_3\text{N}_4$ .

On the other hand, in the synthesis at  $-20^\circ\text{C}$  (Fig.5(A)), the needle-like particles of Ti imide were observed around Si imide particles before heating. This individual precipitate of imide may be caused by the large difference of precipitate rate between Si and Ti imide at  $-20^\circ\text{C}$ . These imide particles were individually crystallized to  $\text{Si}_3\text{N}_4$  and TiN particles by heating as shown Fig.5 (B). The precipitate rates of Si and Ti imide were closer comparatively and the composite structure could be obtained at  $0^\circ\text{C}$ , like as Fig.4 (B). The grain growth of  $\text{Si}_3\text{N}_4$  was retarded by TiN

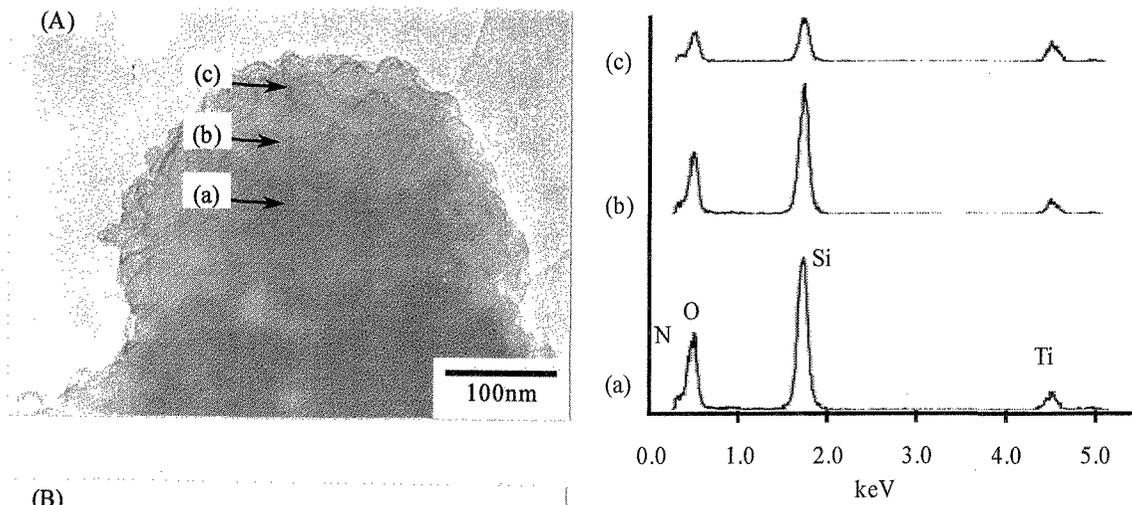


Fig.4 TEM images and EDX profiles of Si<sub>3</sub>N<sub>4</sub>-TiN composite powders synthesized at 0°C. (A) as-precipitated and (B) after heat-treatment at 1500°C.

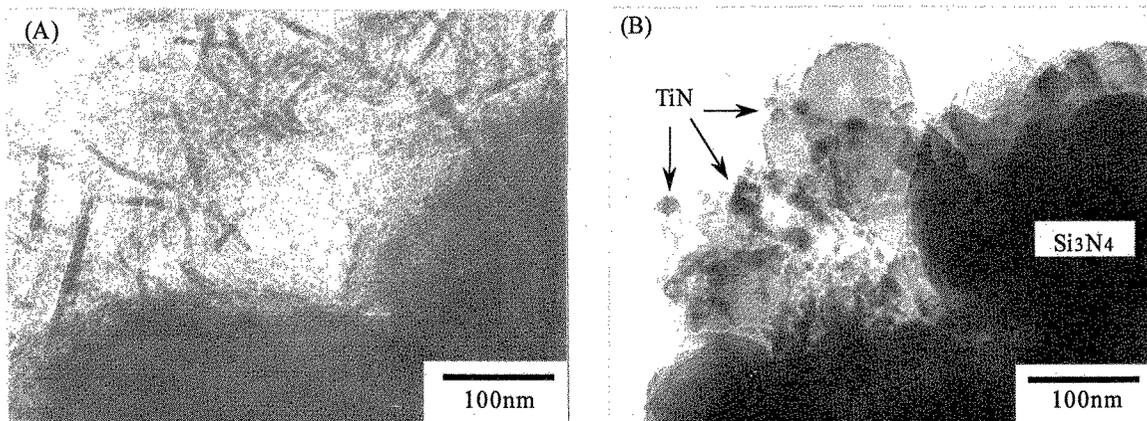


Fig.5 TEM images of Si<sub>3</sub>N<sub>4</sub>-TiN composite powders synthesized at -20°C. (A) as-precipitated and (B) after heat-treatment at 1500°C.

particles in the synthesis at  $-20^\circ\text{C}$ , compared with  $0^\circ\text{C}$ . This may be cause of the weaker peaks of  $\text{Si}_3\text{N}_4$  in the synthesis at  $-20^\circ\text{C}$  than  $0^\circ\text{C}$  as shown in XRD pattern (Fig. 1).

The powders synthesized at  $0^\circ\text{C}$  were hot-pressed for fabrication of sintered bodies. The used powders were heat-treated one at  $1400^\circ\text{C}$ . The particle heated at  $1500^\circ\text{C}$  was not good for sintering because of the square shape of particles. The composite powder was more densified and the relative density was reached to 97%, compared with the monolithic. This behavior was different from that of powders by CVD[4]. The reason was not clarified. During sintering,  $\text{Si}_3\text{N}_4$  crystallized into  $\beta$ -phase. The SEM images are shown in Fig.6. The rod-like grains were observed in  $\text{Si}_3\text{N}_4$ -TiN composite.

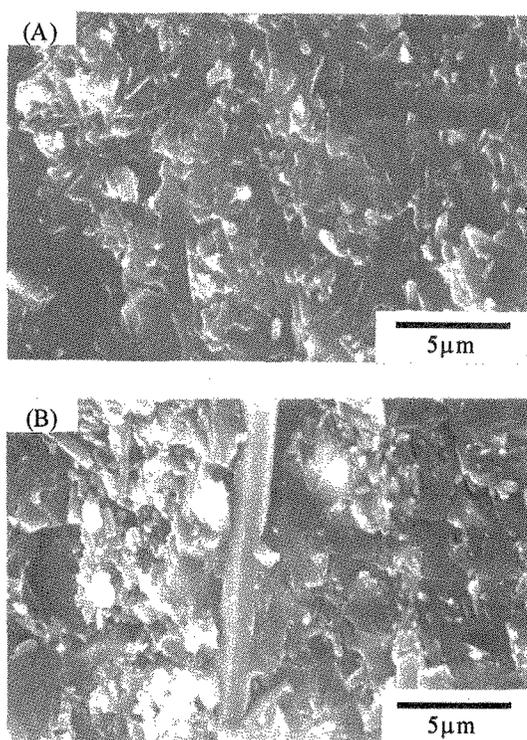


Fig.6 SEM images of monolithic  $\text{Si}_3\text{N}_4$  (A) and  $\text{Si}_3\text{N}_4$ -TiN composite (B) by using powders synthesized at  $0^\circ\text{C}$ .

#### 4. CONCLUSION

Si-Ti composite imide particles were synthesized by liquid phase reaction in  $\text{SiCl}_4$ - $\text{TiCl}_4$ - $\text{NH}_3$  system.

The structures of imide particles were affected by the synthesis temperature. The Si and Ti imides were precipitated individually and the composite powder was not obtained in the synthesis at  $-20^\circ\text{C}$ . However, in the synthesis at  $0^\circ\text{C}$ , the precipitate had a composite structure which Ti-imide segregated on Si-imide surface. TiN was embedded in  $\text{Si}_3\text{N}_4$  particles during decomposition of imide

particles, and the fine composite structure was obtained.

$\text{Si}_3\text{N}_4$ -TiN composite body could be fabricated by hot-pressing of the synthesized  $\text{Si}_3\text{N}_4$ -TiN composite powder. The rod-like grain growth was stimulated by TiN inclusions.

#### REFERENCES

- [1] K. Niihara, *J. Ceram. Soc. Japan*, 99[10], 974-982 (1991).
- [2] J. Hojo, K. Kishi and S. Umebayashi, *Ceramic Transactions 51, American Ceramic Society*, pp.597-601 (1995).
- [3] J. Hojo, *Proc. 4th Nisshin Engineering Particle Technology International Seminar*, pp.9-17 (1995).
- [4] J. Hojo, K. Eto, M. Umezu, K. Kishi and S. Umebayashi, *J. Jpn. Soc. Powder and Powder Metall.*, 45[1], 25-30 (1998).
- [5] T. Yamada, *Am. Ceram. Soc. Bull.*, 72[5], 99-106 (1993).

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