

Rod-like Si_3N_4 grain growth in the sintered body of amorphous Si_3N_4 -BN composite powder with sintering additives

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The sintered structures of amorphous Si_3N_4 -BN composite powder were investigated with sintering aids from the Y_2O_3 - Al_2O_3 and Y_2O_3 - TiO_2 -AlN systems. In the Y_2O_3 - Al_2O_3 system, β - Si_3N_4 and h-BN crystallized during sintering. TiN additionally appeared in the Y_2O_3 - TiO_2 -AlN system. The microstructure of the Si_3N_4 -BN composite was observed by SEM. Flaky BN particles with a length of about 1.0~1.5 μm were observed in the Si_3N_4 matrix. The Si_3N_4 matrix had a fine-grained microstructure in the Y_2O_3 - Al_2O_3 system, whereas rod-like Si_3N_4 grains with a length of 3~10 μm were observed in the Y_2O_3 - TiO_2 -AlN system. The morphology of the TiN particles was observed by TEM. Small TiN particles of about 0.1 μm in diameter were included in large Si_3N_4 grains, but these fine TiN inclusions were a rare case. Large TiN particles of about 1 μm in diameter were located at grain boundaries throughout the sintered body. The thermal shock resistance of Si_3N_4 was improved by the BN inclusions in the Y_2O_3 - Al_2O_3 system. With the Y_2O_3 - TiO_2 -AlN system, the TiN inclusions increased the fracture toughness of the Si_3N_4 -BN composite but the thermal shock resistance was reduced.

Key words: silicon nitride, boron nitride, titanium nitride, composite powder, nanocomposite.

Introduction

Silicon nitride ceramics are excellent in terms of strength, heat resistance and wear resistance, and their application has been developed as engineering materials for such uses as in gas turbine and engine components, etc. However, their fracture toughness and thermal-shock resistance need to be more improved to establish their reliability. Nanocomposites have received a lot of attention as a means of improving their mechanical properties [1]. Hojo *et al.* [2] reported that a Si_3N_4 -BN nanocomposite can be fabricated by the sintering of amorphous Si_3N_4 -BN composite powder prepared by a vapor phase reaction method. A fine dispersion of h-BN was effective in improving the thermal-shock resistance, but the fracture toughness was reduced due to the inhibition of Si_3N_4 grain growth by the BN particles. On the other hand, it was found that TiN inclusions accelerate the growth of rod-like Si_3N_4 grains in a Si_3N_4 -TiN nanocomposite fabricated from composite powder [3]. Ueno *et al.* [4] reported that TiN was finely dispersed in a Si_3N_4 matrix by the in-situ reaction of TiO_2 and AlN included in the sintering aid. Yano *et al.* [5] reported that TiN particles formed in a Si_3N_4 matrix with Y_2O_3 - Al_2O_3 - TiO_2 -AlN as a sintering aid.

The authors reported that TiN formed in the Si_3N_4 -BN composite with Y_2O_3 - TiO_2 -AlN as a sintering aid

and enhanced the rod-like Si_3N_4 grain growth [6], but the mechanism was not clear. In the present paper, to clarify the effect of the inclusion of TiN on the rod-like Si_3N_4 grain growth, the microstructures of Si_3N_4 -BN composites were compared between sintering aids of the Y_2O_3 - Al_2O_3 and Y_2O_3 - TiO_2 -AlN systems, and the mechanical properties (fracture toughness and thermal shock resistance) were measured. The microstructure and properties of monolithic Si_3N_4 were also investigated for comparison.

Experimental

The vapor phase reaction was conducted using a flow-type furnace reactor. Si_3N_4 -BN composite powder was prepared from the SiCl_4 - BCl_3 - NH_3 - H_2 system, and Si_3N_4 powder from the SiCl_4 - NH_3 - H_2 system. The reaction temperature was 1400°C. The by-product, NH_4Cl , was removed by sublimation at 400°C in N_2 . The BN content in the composite powder was determined by a chemical analysis. The sintering aids from the Y_2O_3 (6 wt%)- Al_2O_3 (2 wt%), Y_2O_3 (6 wt%)- TiO_2 (2 wt%) and Y_2O_3 (6 wt%)- TiO_2 (2~3 wt%)-AlN(1.6 wt%) systems were added to the powders by dry milling. Hot pressing was carried out for 2h at 1800°C and 50 MPa in N_2 .

The crystalline phases were identified by X-ray diffraction (XRD). The microstructure was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The specimens for SEM were polished and plasma-etched with CF_4 containing 8% O_2 . The thin specimens for TEM were prepared by

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polishing, dimple-grinding and final Ar ion-milling. Energy-dispersive X-ray microanalysis (EDX) was also carried out in the TEM observations. The fracture toughness was measured by the Vickers indentation technique (load: 10 kg) and calculated using Niihara's equation [7]. The thermal shock resistance was evaluated by a quenching method using water at room temperature, in which cracks on the specimen surface were observed with an optical microscope. The test was repeated for each sample with increasing temperature at about 25°C intervals.

Results and Discussion

Crystalline phases of monolithic Si_3N_4 and Si_3N_4 -BN composites

Fine Si_3N_4 powder and Si_3N_4 -BN composite powder were produced by the vapor phase reaction method. Figure 1 shows the SEM image of the Si_3N_4 -BN composite particles. The particles were spherical and about 0.1 μm in size. Si_3N_4 particles had a similar morphology. The powders were all amorphous. Hojo *et al.* [8] reported that the composite powder was not a mixture of Si_3N_4 and BN particles, but Si_3N_4 and BN were mixed on nearly a molecular level in each particle.

Figure 2(A) shows the XRD patterns of monolithic Si_3N_4 sintered with additives from the Y_2O_3 - Al_2O_3 , Y_2O_3 - TiO_2 -AlN and Y_2O_3 - TiO_2 systems. The amorphous powder crystallized into β - Si_3N_4 during sintering. A small peak of Si was detected. This may be caused by partial decomposition of amorphous Si_3N_4 . Compared to the Y_2O_3 - Al_2O_3 system, a small peak of TiN additionally appeared in the Y_2O_3 - TiO_2 -AlN and Y_2O_3 - TiO_2 systems. A previous paper [6] described that amorphous Si_3N_4 reacted with TiO_2 to form $\text{Si}_2\text{N}_2\text{O}$ and TiN at 1400°C~1600°C. $\text{Si}_2\text{N}_2\text{O}$ disappeared at 1800°C. In the Y_2O_3 - TiO_2 system, $\text{Si}_2\text{N}_2\text{O}$ is thought to decompose to Si_3N_4 and SiO_2 . In the Y_2O_3 - TiO_2 -AlN system, $\text{Si}_2\text{N}_2\text{O}$ can react with AlN to form Si_3N_4 and Al_2O_3 . SiO_2 and Al_2O_3 may dissolve into a liquid phase in the sintering

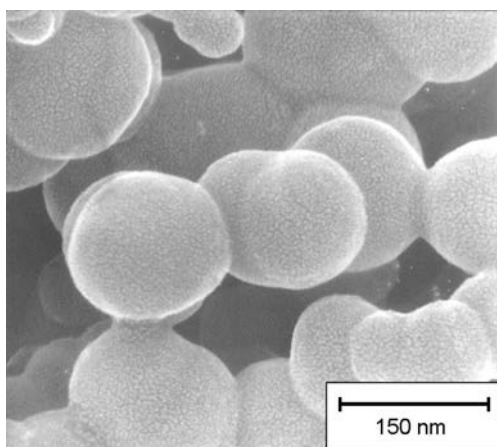


Fig. 1. SEM image of Si_3N_4 -BN composite powder.

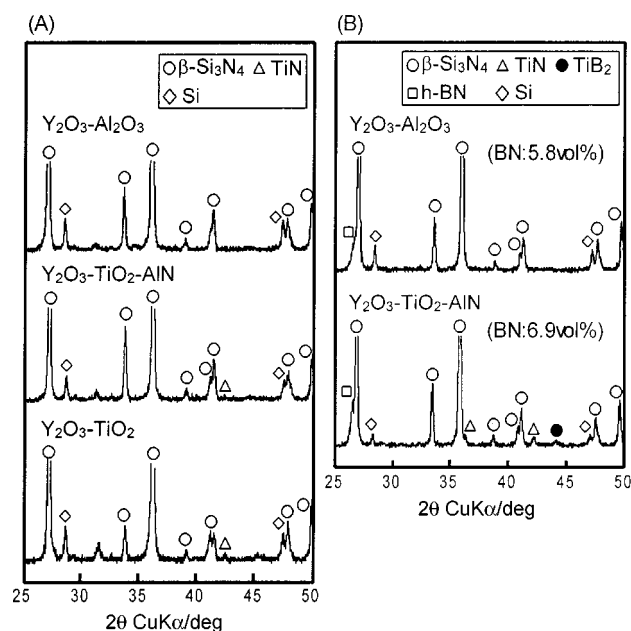


Fig. 2. XRD patterns of (A) monolithic Si_3N_4 and (B) Si_3N_4 -BN composites sintered with additives from the Y_2O_3 - Al_2O_3 , Y_2O_3 - TiO_2 -AlN and Y_2O_3 - TiO_2 systems.

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Figure 2(B) shows the XRD patterns of the Si_3N_4 -BN composite sintered with additives from the Y_2O_3 - Al_2O_3 and Y_2O_3 - TiO_2 -AlN systems. β - Si_3N_4 and h-BN crystallized and a small amount of silicon formed in both systems. In the case of Y_2O_3 - TiO_2 -AlN system, small peaks of TiN and TiB_2 were detected. The formation of TiN may occur by the same mechanism as in monolithic Si_3N_4 . The formation of TiB_2 results from the reaction between TiO_2 or TiN with BN.

Microstructure of the sintered body

Figure 3 shows the SEM images of the etched surface of monolithic Si_3N_4 sintered with additives from the Y_2O_3 - Al_2O_3 , Y_2O_3 - TiO_2 -AlN and Y_2O_3 - TiO_2 systems. In the case of the Y_2O_3 - Al_2O_3 system, the sintered body had a fine-grained microstructure, including small needle-like grains. In the case of the Y_2O_3 - TiO_2 -AlN system, rod-like Si_3N_4 grains with a length of 3~10 μm grew throughout the sintered body. On the other hand, in the Y_2O_3 - TiO_2 system, rod-like Si_3N_4 grains with a length of about 10 μm were observed in a fine Si_3N_4 matrix, but the number of rod-like grains was less than in the Y_2O_3 - TiO_2 -AlN system. These results suggest that rod-like Si_3N_4 grain growth was stimulated by the TiO_2 addition and that the Y_2O_3 - TiO_2 -AlN system was more effective than the Y_2O_3 - TiO_2 system. There are two possible reasons for rod-like Si_3N_4 grain growth in these systems. One is that TiN particles act as nuclei for Si_3N_4 grain growth. It is well known that the densification and grain growth of Si_3N_4 occur by a liquid-phase mechanism. During the dissolution-precipitation process, TiN might behave as a nucleus to initiate the

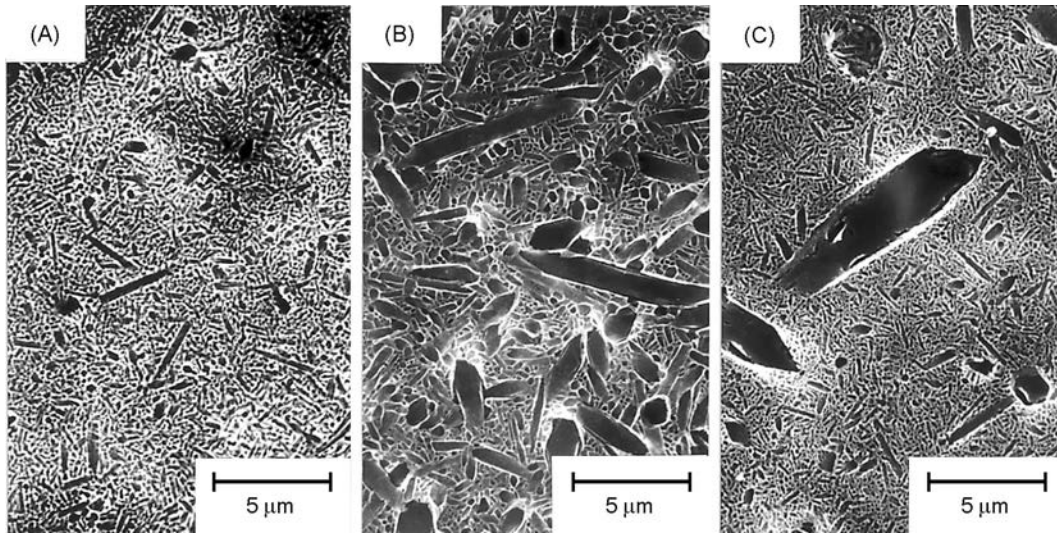


Fig. 3. SEM images of etched surface of monolithic Si_3N_4 sintered with additives from the (A) $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$, (B) $\text{Y}_2\text{O}_3\text{-TiO}_2\text{-AlN}$ and (C) $\text{Y}_2\text{O}_3\text{-TiO}_2$ systems.

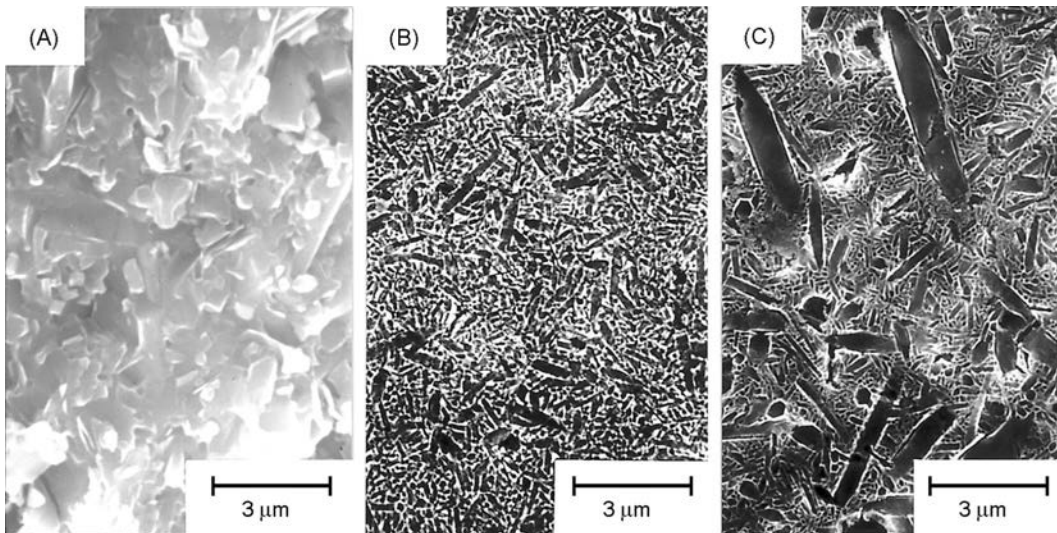


Fig. 4. SEM images of fracture surface and etched surface of $\text{Si}_3\text{N}_4\text{-5.4 vol\%BN}$ composites sintered with additives from the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{-TiO}_2\text{-AlN}$ systems. (A) fracture surface, $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ (B) etched surface, $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ (C) etched surface, $\text{Y}_2\text{O}_3\text{-TiO}_2\text{-AlN}$.

growth of rod-like Si_3N_4 grains. Another possibility is that the composition of the grain boundary phase was changed by the TiO_2 addition.

The fracture surface of the $\text{Si}_3\text{N}_4\text{-BN}$ composite was observed by SEM (Figure 4(A)). Flaky BN particles with a length of about $1.0\sim 1.5\ \mu\text{m}$ were observed in the Si_3N_4 matrix with the use of the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{-TiO}_2\text{-AlN}$ systems [6]. Figure 4(B) shows the SEM image of an etched surface of a $\text{Si}_3\text{N}_4\text{-BN}$ composite in the $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ system. The growth of needle-like Si_3N_4 grains was more noticeable compared to monolithic Si_3N_4 , but the grain size was small. On the other hand, in the $\text{Y}_2\text{O}_3\text{-TiO}_2\text{-AlN}$ system, rod-like Si_3N_4 grains with a length of $3\sim 10\ \mu\text{m}$ were observed as well as in monolithic Si_3N_4 . These results indicate that the growth of rod-like Si_3N_4 grains was also stimulated by the TiO_2 addition in the $\text{Si}_3\text{N}_4\text{-BN}$ system.

Morphology of the TiN particles

The morphology of TiN particles was observed by TEM. Figure 5 shows a TEM image of monolithic Si_3N_4 sintered with additives from the $\text{Y}_2\text{O}_3\text{-TiO}_2\text{-AlN}$ system. Large and small particles with darker contrast were observed as shown by an arrow. Small particles with a size of $0.1\ \mu\text{m}$ were included within large Si_3N_4 grains, and large particles with a size of $1\ \mu\text{m}$ were located at the grain boundaries. By EDX analysis, Ti and N were detected in these particles, indicating that these particles were TiN. Large TiN particles were observed throughout the sintered body, but the fine TiN inclusions were a rare case. It is difficult to postulate that the TiN particles act as nuclei because the TiN particles were rarely observed in Si_3N_4 grains. Therefore, the rod-like Si_3N_4 grain growth may be related to a change in liquid phase composition at the grain boundaries by the TiO_2 addition.

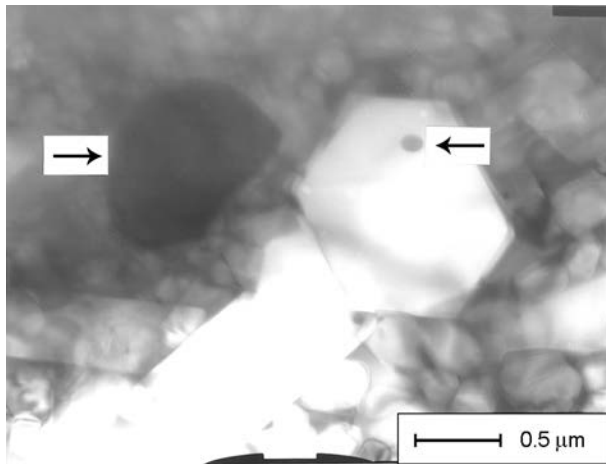


Fig. 5. TEM image of monolithic Si_3N_4 sintered with additives from the Y_2O_3 - TiO_2 -AlN system.

Fracture toughness and thermal shock resistance

The mechanical properties of monolithic Si_3N_4 and Si_3N_4 -BN composite are summarized in Table 1. In monolithic Si_3N_4 sintered with the Y_2O_3 - Al_2O_3 sintering aid, the fracture toughness was $6.3 \text{ MPa}\cdot\text{m}^{1/2}$ and the thermal-shock resistance was 700°C . It has been reported that the addition of h-BN particles to Si_3N_4 is effective in improving the thermal-shock resistance because the thermal stress can be absorbed by the low elastic modulus h-BN [8]. In the present work with Y_2O_3 - Al_2O_3 as a sintering aid, the thermal-shock resistance of the Si_3N_4 -BN composite increased to 770°C , but the fracture toughness decreased to $5.5 \text{ MPa}\cdot\text{m}^{1/2}$. On the other hand, with the Y_2O_3 - TiO_2 -AlN sintering aid, the fracture toughness increased to $6.6 \text{ MPa}\cdot\text{m}^{1/2}$, but the thermal-shock resistance decreased to 700°C . The improvement of fracture toughness may be due to crack deflection by rod-like Si_3N_4 grains. The decrease in thermal shock resistance may be caused by large TiN inclusions because TiN has a large thermal expansion coefficient. A fine dispersion of TiN is required to achieve excellent mechanical properties.

Conclusions

Fine Si_3N_4 -BN composite powder was prepared by a vapor phase reaction method. When Y_2O_3 - TiO_2 -AlN was used as sintering aid, TiN formed in addition to β -

Table 1. Mechanical properties of monolithic Si_3N_4 and Si_3N_4 -BN composites

Sample	Sintering aid	BN (vol%)	Properties of sintered body		
			dr (%)	K_{IC} ($\text{MPa}\cdot\text{m}^{1/2}$)	ΔT ($^\circ\text{C}$)
Si_3N_4	6 wt% Y_2O_3 -2 wt% Al_2O_3	0	97.4	6.3	700
	6 wt% Y_2O_3 -2 wt% Al_2O_3	5.4	96.1	5.5	775
Si_3N_4 -BN	6 wt% Y_2O_3 -2 wt% TiO_2 -1.6 wt% AlN	5.4	96.7	6.6	700

dr: relative density. K_{IC} : fracture toughness.

ΔT : critical temperature difference for crack initiation.

Si_3N_4 and h-BN. The addition of TiO_2 and AlN to the Y_2O_3 sintering aid enhanced the rod-like grain growth even in the Si_3N_4 -BN composite. The rod-like Si_3N_4 grain growth may be related to a liquid composition change in the grain boundary phase. The thermal shock resistance of Si_3N_4 was improved by the BN inclusions in the Y_2O_3 - Al_2O_3 system. With the Y_2O_3 - TiO_2 -AlN system, the TiN inclusions increased the fracture toughness of the Si_3N_4 -BN composite but decreased the thermal shock resistance.

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