

Synthesis of Si_3N_4 composite nano-powders and evaluation of sintered bodies

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Fine Si_3N_4 powder, Si_3N_4 -TiN composite powder and Si_3N_4 -BN-TiN composite powder were prepared by a vapor phase reaction method, and hot-pressed to investigate the effects of TiN inclusion in Si_3N_4 -TiN composites and BN inclusion in Si_3N_4 -BN-TiN composites on the microstructure and mechanical properties of sintered bodies. The prepared powders were fine with a size of about 80-100 nm. Hot pressing was carried out for 2h at 1800°C and 50 MPa in N_2 with 6 wt% Y_2O_3 and 2 wt% Al_2O_3 as sintering aids. When the content of TiN was small, Si_3N_4 -TiN composites included rod-like Si_3N_4 grains dispersed in a fine Si_3N_4 matrix, having a high thermal shock resistance whilst retaining their fracture toughness. The thermal shock resistance of Si_3N_4 -TiN composites was not improved by addition of the BN and the fracture toughness was reduced.

Key words: silicon nitride, nano-composite, composite powder, thermal shock resistance, fracture toughness.

Introduction

Silicon nitride ceramics are the most balanced materials among structural ceramics in terms of strength and toughness. However, the brittleness and the lack of reliability, compared to metallic materials, limit the in applications. In order to solve these problems, compositing techniques have been studied. A typical example is Si_3N_4 -SiC nano-composites as reported by Niihara *et al.* [1]. Hojo *et al.* have studied Si_3N_4 -TiN nano-composites and Si_3N_4 -BN nano-composites fabricated by sintering of composites powders prepared by a vapor phase reaction method [2]. The fine dispersion of TiN in a Si_3N_4 matrix was effective in improving the fracture toughness owing to crack deflection by large rod-like Si_3N_4 grains grown with TiN inclusions, however, the thermal shock resistance was reduced due to the gap in thermal expansion coefficients between Si_3N_4 and TiN. On the other hand, Si_3N_4 -BN nano-composites have an excellent thermal shock resistance because the thermal stress can be absorbed by the low elastic coefficient h-BN.

We have tried to improve the thermal shock resistance of Si_3N_4 -TiN nano-composites without reducing their high fracture toughness by the addition of BN which is effective in improving the thermal shock resistance, and limiting the content of TiN which is a factor in decreasing the thermal shock resistance.

Experimental

A vapor phase reaction was conducted using a flow-type furnace reactor. Si_3N_4 powder, Si_3N_4 -TiN composite powder and Si_3N_4 -BN-TiN composite powder were prepared in the SiCl_4 - NH_3 - H_2 system, the SiCl_4 - TiCl_4 - NH_3 - H_2 system and the SiCl_4 - BCl_3 - TiCl_4 - NH_3 - H_2 system, respectively. The reaction temperature was 1400°C. NH_4Cl included in the produced powder was removed by sublimation at 400°C in N_2 . The BN content was determined by chemical analysis, and the TiN content by energy dispersive X-ray analysis. Particle morphology was observed by transmission electron microscopy (TEM).

The powders were hot-pressed for 2h at 1800°C and 50 MPa in N_2 with Y_2O_3 - Al_2O_3 as sintering aids. The crystalline phases were identified by X-ray diffraction (XRD). The microstructure was observed by scanning electron microscopy (SEM). The specimens for SEM were polished and plasma-etched with CF_4 containing 8% O_2 . The fracture toughness was measured by the Vickers indentation technique (load: 10 kg) and calculated using Niihara *et al.*'s equation [3]. The thermal shock resistance was evaluated by a water quenching method at room temperature, in which cracks on the disk surface were observed with an optical microscope. This test was repeated for each sample with increasing temperature at about 25°C intervals.

Results and Discussion

Characterization of synthesized powders

Fine powders of the Si_3N_4 , Si_3N_4 -TiN system and the Si_3N_4 -BN-TiN system were produced by a vapor phase reaction. A TEM image of the Si_3N_4 -BN-TiN composite powder is shown as an example in Fig. 1. The particles

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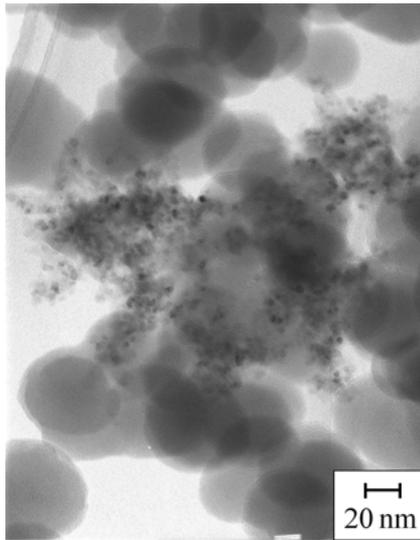


Fig. 1. TEM image of Si_3N_4 -BN-TiN composite powder.

were spherical and about 80-100 nm in size. Also, nano-size TiN particles with a size below 10 nm were observed, which was confirmed from electron diffraction patterns.

Crystalline phases and microstructure of sintered bodies

Si_3N_4 and BN were amorphous, and TiN was crystalline in the as-prepared powder. Figure 2 shows XRD patterns of sintered bodies. The peaks from $\beta\text{-Si}_3\text{N}_4$ were observed in all samples. In the Si_3N_4 -TiN composite, the peaks from TiN were not detected at a small TiN content (0.9 vol% TiN) and appeared with increasing TiN content as seen in Fig. 2. In the Si_3N_4 -BN-TiN

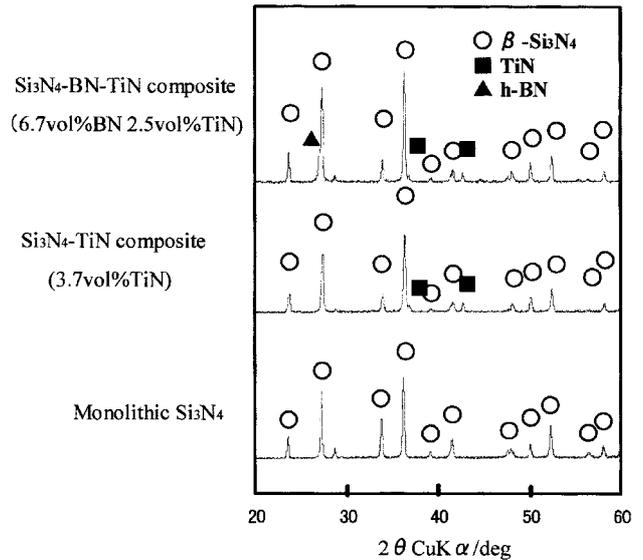


Fig. 2. XRD patterns of sintered bodies.

composite, the peak from BN was observed in addition to that from TiN.

Microstructure of sintered bodies

Figure 3 shows SEM images of sintered textures in monolithic Si_3N_4 and Si_3N_4 -TiN composites. Figure 4 shows SEM images of sintered textures of Si_3N_4 -BN-TiN composites. Large rod-like Si_3N_4 grains with a length of about 3-12 μm were observed in the sintered texture of monolithic Si_3N_4 . In the Si_3N_4 -0.9 vol% TiN composite, rod-like Si_3N_4 grains were dispersed in a fine Si_3N_4 matrix without interference between rod-like grains. When the content of TiN was increased, rod-like Si_3N_4 grains grew significantly. It was thought that

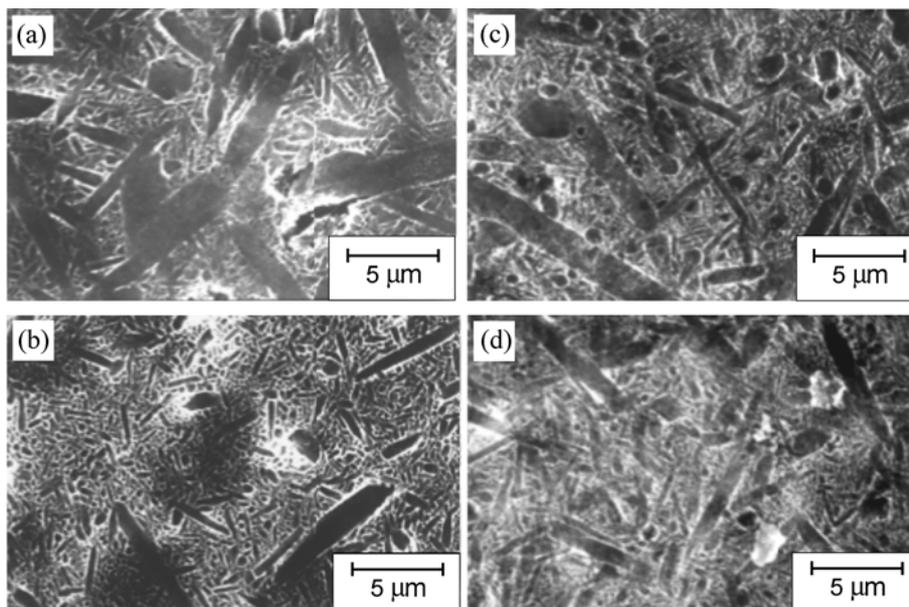


Fig. 3. SEM images of sintered textures of monolithic Si_3N_4 and Si_3N_4 -TiN composites. (a) monolithic Si_3N_4 , (b) Si_3N_4 -0.9 vol%TiN composite, (c) Si_3N_4 -3.7 vol%TiN composite, (d) Si_3N_4 -8.4 vol%TiN composite.

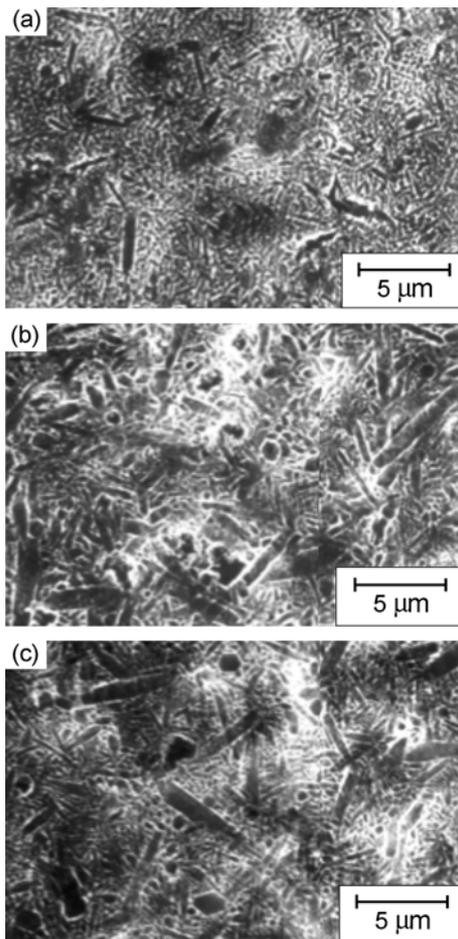


Fig. 4. SEM images of sintered textures of Si_3N_4 -BN-TiN composite. (a) Si_3N_4 -6.7 vol%BN-2.5 vol%TiN composite, (b) Si_3N_4 -5.1 vol%BN-4.1 vol%TiN composite, (c) Si_3N_4 -3.1 vol%BN-5.1 vol%TiN composite.

the texture changed into fine one because of an inhibition effect of grain growth by the TiN particles. A previous study explained that Si_3N_4 grain growth was enhanced by dissolution of TiN in the liquid phase of the oxide sintering aid [4]. According to the present results, large rod-like Si_3N_4 grains were observed in monolithic Si_3N_4 and at large TiN contents. Maybe, at 0.9 vol% TiN, the pinning and enhancing effects of TiN in grain growth were balanced, giving the fine structure.

In the Si_3N_4 -BN-TiN composite, the microstructure was finer than that of the Si_3N_4 -TiN composite because BN inclusions retarded the Si_3N_4 grain growth. In this system also, the microstructure was fine at a small TiN content, but included large rod-like Si_3N_4 grains with increasing TiN content.

Fracture toughness and thermal shock resistance

Mechanical properties are summarized in Fig. 5. The thermal shock resistance and fracture toughness of monolithic Si_3N_4 were 625°C and $7.0 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. The addition of 0.9 vol% TiN led to a drastic improvement of the thermal shock resistance (775°C)

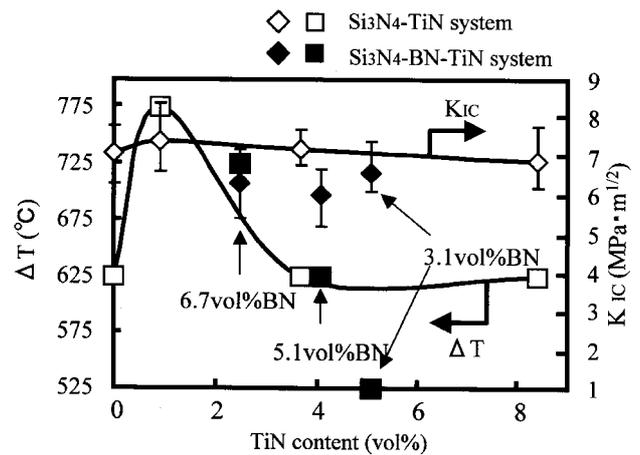


Fig. 5. Mechanical properties of sintered bodies. K_{1C} : fracture toughness, ΔT : thermal shock resistance (critical temperature differences of crack initiation).

without reducing K_{1C} . These results suggest that the improvement of the thermal shock resistance results from the fine microstructure and decreasing TiN content. Although the microstructure was fine, the K_{1C} was retained because of crack deflection by the rod-like Si_3N_4 dispersed in the fine structure. When the content of TiN was increased, the thermal shock resistance decreased around 625°C . Large rod-like Si_3N_4 grains and large TiN grains may cause this decrease because TiN grains have a large thermal expansion coefficient and large rod-like Si_3N_4 grains have different thermal expansion coefficients along the a and c axes.

In Si_3N_4 -BN-TiN composites, the thermal shock resistance tended to decline with increasing TiN content and was not improved compared to Si_3N_4 -TiN composites. Also, the fracture toughness of Si_3N_4 -BN-TiN composites tell below the value of Si_3N_4 -TiN composites. Thus, the addition of BN to Si_3N_4 -TiN composites did not lead to an improvement in the thermal shock resistance because the good effects of BN are counteracted by the inclusion of TiN grains and large rod-like Si_3N_4 grains.

Conclusion

Si_3N_4 powder, Si_3N_4 -TiN composite powder and Si_3N_4 -BN-TiN composite powder were prepared by a vapor phase reaction method. The powders were composed of spherical particles with a size below 100 nm. Both in the Si_3N_4 -TiN composites and in the Si_3N_4 -BN-TiN composites, the texture was a fine microstructure at a small TiN content and large rod-like Si_3N_4 grains were observed with increasing TiN content. Limiting the content of TiN in Si_3N_4 -TiN composites led to an improvement of the thermal shock resistance without reducing the high fracture toughness. Addition of BN to Si_3N_4 -TiN composites did not lead to an improvement of the thermal shock resistance and caused a decline in the fracture toughness.

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