

## Development of CNT-dispersed $\text{Si}_3\text{N}_4$ Ceramics by Adding Lower Temperature Sintering Aids

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### ABSTRACT

The study to give electrical conductivity by dispersing carbon nanotubes (CNT) into silicon nitride ( $\text{Si}_3\text{N}_4$ ) ceramics has been carried out in recent years. However, the density and the strength of  $\text{Si}_3\text{N}_4$  ceramics were degraded and CNTs disappeared after firing at high temperatures because CNTs prevent  $\text{Si}_3\text{N}_4$  from densification and there is a possibility that CNTs react with  $\text{Si}_3\text{N}_4$  or  $\text{SiO}_2$ . In order to suppress the reaction and the disappearance of CNTs, lower temperature densification is needed. In this study,  $\text{HfO}_2$  and  $\text{TiO}_2$  was added to  $\text{Si}_3\text{N}_4$ - $\text{Y}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ - $\text{AlN}$  system to fabricate CNT-dispersed  $\text{Si}_3\text{N}_4$  ceramics at lower temperatures.  $\text{HfO}_2$  promotes the densification of  $\text{Si}_3\text{N}_4$  and prevents CNT from disappearance. As a result, the sample by adding  $\text{HfO}_2$  and  $\text{TiO}_2$  fired at lower temperatures showed higher electrical conductivity and higher bending strength. It was also shown that the mechanical and electrical properties depended on the quantity of the added CNTs.

**Key words :** Silicon nitride, Carbon nanotube, Hafnium oxide, Titanium oxide, Electrical conductivity

### 1. Introduction

**S**ilicon nitride ( $\text{Si}_3\text{N}_4$ ) ceramics have excellent mechanical as well as chemical, thermal properties, for example, they have high strength, toughness, hardness, corrosion resistance, heat resistance, heat conductivity, and insulation strength. Hence, they have been used in structural components, bearings, engine parts, gas turbines, and cutting tools, among other devices.<sup>1-3)</sup> Silicon nitride itself is an insulator, and hence, conventional  $\text{Si}_3\text{N}_4$  ceramics are also insulators. Dust adheres easily onto the surface of such  $\text{Si}_3\text{N}_4$  ceramics owing to static electricity. As a result, they sometimes cause the breakdown of a system and reduce its lifetime. For this reason, these ceramics need to have electrical conductivity.

Carbon nanotubes (CNTs) have been used as fillers owing to their electrical conductivity, high elastic modulus, high strength, and high aspect ratio.<sup>4-6)</sup> When CNTs are dispersed in a sintered body, electrical conduction paths are formed by a small quantity of the CNTs. However, CNTs inhibit densification during the sintering process. Furthermore in the case of CNT-dispersed  $\text{Si}_3\text{N}_4$  ceramics, CNTs react with  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  at high temperatures to generate gases such as nitrogen, carbon monoxide, and carbon dioxide. The formation of these gases also suppresses the densification of  $\text{Si}_3\text{N}_4$  ceramics, and the added CNTs disappear during the firing process. To prevent the CNTs from reacting and disappearing, densi-

fication needs to be carried out at a low temperature. In a previous study on CNT-dispersed  $\text{Si}_3\text{N}_4$  ceramics, many researchers applied various sintering processes like spark plasma sintering and hot pressing to obtain dense ceramics.<sup>7-10)</sup> Dense CNT-dispersed  $\text{Si}_3\text{N}_4$  ceramics was fabricated using  $\text{TiO}_2$  as a sintering aid in our previous study,<sup>11-13)</sup> because  $\text{TiO}_2$  improves densification of  $\text{Si}_3\text{N}_4$ .<sup>14)</sup> In this study, we focused on simultaneous addition of  $\text{HfO}_2$  and  $\text{TiO}_2$  as a sintering aid because it promotes the densification of  $\text{Si}_3\text{N}_4$  on account of the reaction between  $\text{HfO}_2$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{Si}_2\text{O}_3$  at around 1600°C to generate a liquid phase.<sup>15,16)</sup>  $\text{HfO}_2$  should be able to prevent CNTs from disappearing because it reportedly prevents the oxidation of carbon and SiC.<sup>10,17,18)</sup> Therefore, it is expected that as an additive,  $\text{HfO}_2$  and  $\text{TiO}_2$  makes it possible for CNT-dispersed  $\text{Si}_3\text{N}_4$  ceramics to be densified using gas-pressure sintering at temperatures lower than those used with other sintering aids.

The purpose of this study is to reveal the effect of adding  $\text{HfO}_2$  and  $\text{TiO}_2$  as a sintering aid during fabrication on the electrical and mechanical properties of CNT-dispersed  $\text{Si}_3\text{N}_4$  ceramics.

### 2. Experimental Procedure

Fine high-purity powders of  $\text{Si}_3\text{N}_4$  (SN-E-10, Ube Industries, Ltd., Japan),  $\text{Y}_2\text{O}_3$  (RU, Shin-Etsu Chemical Co., Ltd., Japan),  $\text{Al}_2\text{O}_3$  (AKP-30, Sumitomo Chemical Co., Ltd., Japan),  $\text{AlN}$  (F grade, Tokuyama Co., Japan),  $\text{HfO}_2$  (HFO01PB, Kojundo Chemical Laboratory Co., Ltd., Japan), and  $\text{TiO}_2$  (R-11-P, Sakai Chemical Industry Co., Ltd., Japan), were used as raw materials. The multiwall carbon nanotubes used in this

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study (VGCFs, Showa Denko K.K., Japan) had diameters of 60 nm and lengths of 6  $\mu\text{m}$ .  $\text{Si}_3\text{N}_4$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{AlN}$ ,  $\text{HfO}_2$ , and  $\text{TiO}_2$  powders were weighed in the proportion 92:5:3:5:1.5:3.5, in that order. The samples containing  $\text{HfO}_2$  and  $\text{TiO}_2$  were labeled sample HT and sample T, respectively. CNTs were added in the 0 to 1.0 wt% range. The CNTs and a dispersant (Seruna E503, Chukyo Yushi Co., Ltd., Japan) were placed in ethanol. After ultrasonication for 20 min, the  $\text{Si}_3\text{N}_4$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{AlN}$ ,  $\text{HfO}_2$  and  $\text{TiO}_2$  powders were added to the CNT slurry with 2 wt% of the dispersant. Ball milling was carried out at 110 rpm for 48 h using 5 mm sialon balls for mixing the powders. The powder mixtures were obtained by evaporating the ethanol. Paraffin (4 wt%, melting point: 46–48°C, Junsei Chemical Co., Japan) and bis(2-ethylhexyl) phthalate (2 wt%, Wako Pure Chemical Industries, Ltd., Japan) were added as the binder and the lubricant, respectively, to make granules by sieving the mixed powder using a nylon mesh with openings of 250  $\mu\text{m}$ . The granules were molded into dimensions of 35 mm  $\times$  45 mm  $\times$  5 mm by uniaxial pressing at 50 MPa, followed by cold isostatic pressing at 200 MPa. The organic binder was eliminated at 500°C for 3 h at a 4 L/min  $\text{N}_2$  flow. After dewaxing, the green bodies were fired at 1600, 1650, 1700 and 1750°C for 2 h in 0.9 MPa  $\text{N}_2$  using a gas-pressure sintering (GPS) furnace (Himulti 5000, Fujidempa Kogyo Co., Ltd., Japan). For more densification, the gas-pressure sintered samples were densified by hot isostatic pressing (HIP) at 1700°C for 1 h under 100 MPa  $\text{N}_2$ . The density of the samples was measured by the Archimedes method. The phase present in the samples was identified by the X-ray diffraction method (Multiflex, Rigaku Co., Japan). The microstructure was observed using a scanning electron microscope (JSM-5200, JEOL Ltd., Japan). The electrical conductivity of the samples was measured by the four-terminal method, and the bending strength was measured by performing a three-point bending test with a span of 30 mm.

### 3. Results and Discussion

Fig. 1 shows the SEM images of the etched surface and the fracture surface of sample HT containing 1.0 wt% of CNT and fired at 1600°C. CNT dispersed- $\text{Si}_3\text{N}_4$  ceramics were densified well at low GPS temperature. The tuberous particles observed to project from the fracture surface are CNTs. Many CNTs remained in the sintered body, which had the same microstructure as the CNT-dispersed  $\text{Si}_3\text{N}_4$  ceramics developed in our previous research.<sup>10–13)</sup> The CNTs dispersed well and existed randomly; thus, the formation of electrical conduction paths could be expected. Apparently,  $\text{HfO}_2$  and  $\text{TiO}_2$  played an important role in causing CNTs to remain in the sintered body even after sintering.

Fig. 2 shows the relative density of the sintered specimens. The relative densities of all the specimens were very high. They were above 93% after GPS and above 96% after HIP. As shown in this figure, the relative density decreased with an increase in the quantity of CNTs; this is similar to the tendency of the relative density observed in the previous

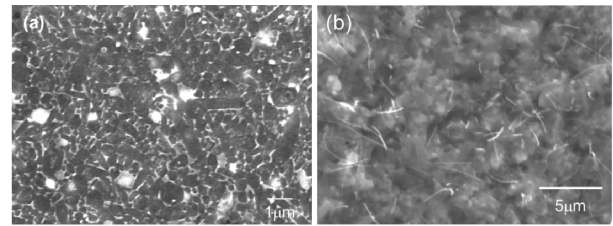


Fig. 1. SEM images of CNT-dispersed  $\text{Si}_3\text{N}_4$  ceramics fired at 1600°C (a) etched surface, (b) fracture surface.

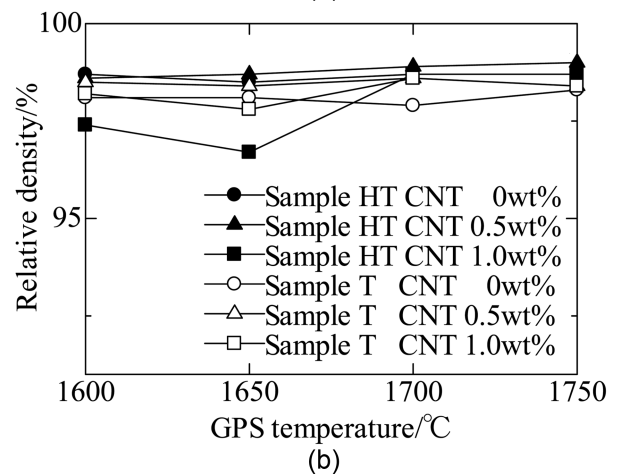
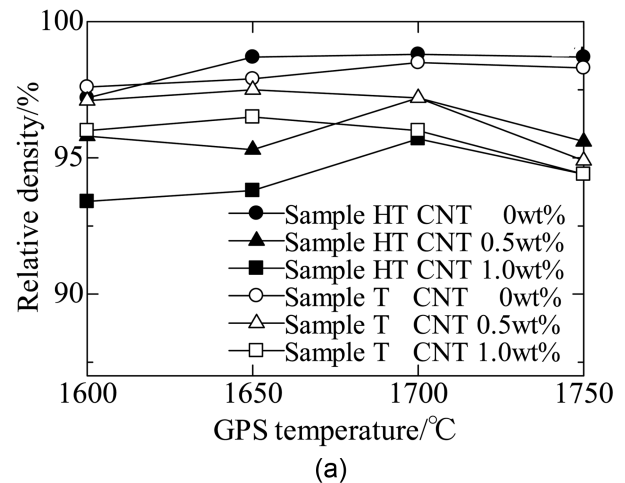


Fig. 2. Relative density of CNT-dispersed  $\text{Si}_3\text{N}_4$  ceramics fired at 1600–1750°C (a) GPS, (b) GPS+HIP.

research on CNT-dispersed  $\text{Si}_3\text{N}_4$  ceramics.<sup>10–13)</sup> The reason for the degradation of the density was that the CNTs hampered the densification of  $\text{Si}_3\text{N}_4$  by forming gases after reacting with  $\text{Si}_3\text{N}_4$  or  $\text{SiO}_2$ .

Fig. 3 shows the bending strength of the sintered specimens. As shown in this figure, the bending strength decreases with an increase in the quantity of CNTs because the several gases generated by the reaction between the CNTs and  $\text{Si}_3\text{N}_4$  or  $\text{SiO}_2$  possibly suppress densification and large agglomerates of CNTs act as fracture origins. Samples HT fired at 1750°C had bending strengths of 985 MPa and 814 MPa after the addition of 0.5 and 1.0 wt% CNT, respectively. These values were higher than the bending strength of

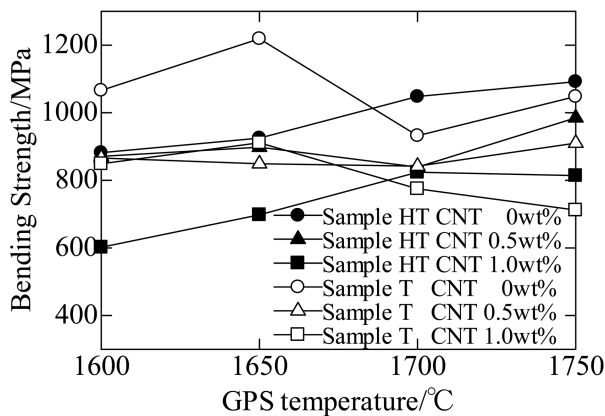


Fig. 3. Bending strength of CNT-dispersed Si<sub>3</sub>N<sub>4</sub> ceramics fired at 1600-1750°C.

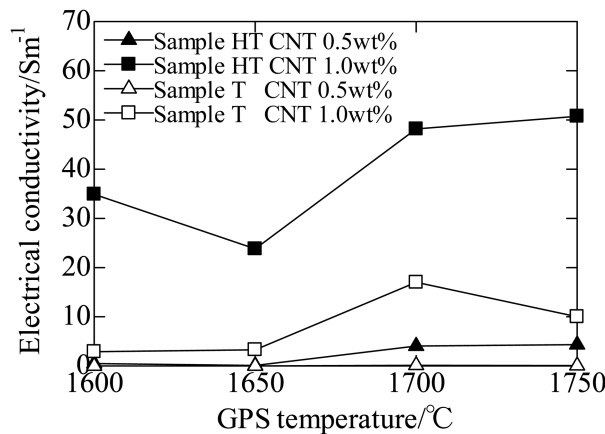


Fig. 4. Electrical conductivity of CNT-dispersed Si<sub>3</sub>N<sub>4</sub> ceramics fired at 1600-1750°C.

sample T, fabricated by adding the same amount of CNTs. In particular, the bending strength of sample HT by adding 0.5 wt% CNT was higher than those of sample T containing 0.5 and 1.0 wt% CNT and fired at any GPS temperature.

Fig. 4 shows the electrical conductivity of the sintered specimens. The electrical conductivity of sample HT increased with an increase in the quantity of CNTs and the GPS temperature for 0.5 and 1.0 wt% CNT addition. Sample T, with 0.5 wt% CNT addition, was an insulator, regardless of the GPS temperature. Sample HT showed higher electrical conductivity than sample T. Although sample T, fabricated by adding 0.5 wt% CNT, was an insulator, sample HT, fabricated by adding the same quantity of CNTs, showed electrical conductivity. The electrical conductivity of sample HT, fabricated by adding 1.0 wt% CNT and fired at 1750°C, was 51 S/m. This value was three times as high as that of sample T, fabricated by adding the same amount of CNT and fired at 1700°C. Shimada reported that HfO<sub>2</sub> improved the oxidation resistance of silicon carbide compositionally graded graphite.<sup>17,18)</sup> In our study, sample HT had higher electrical conductivity than sample T. This was probably a result of the prevention of the reaction of CNTs by HfO<sub>2</sub><sup>10)</sup>, just as in the study conducted by Shimada. The HfO<sub>2</sub> additive improved

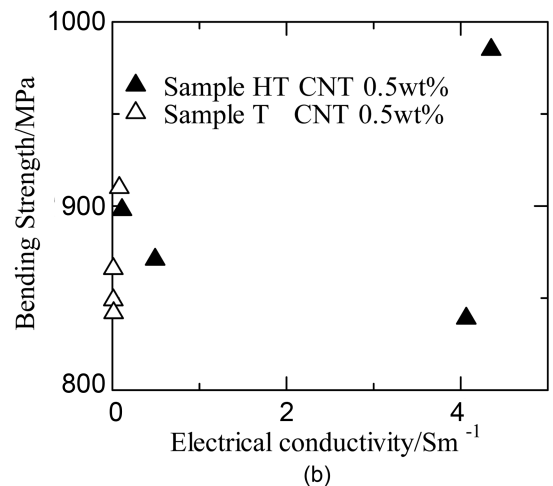
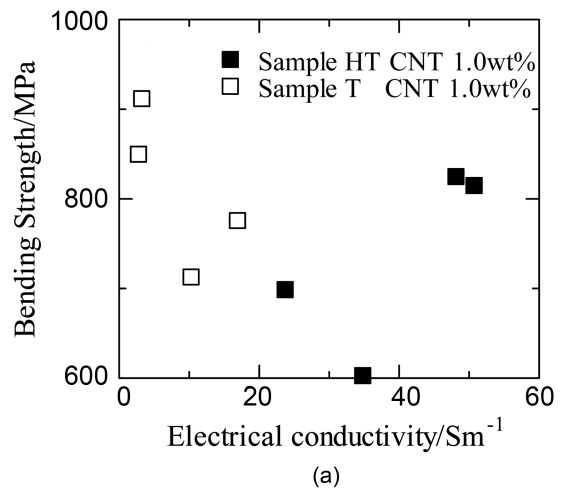


Fig. 5. Relationship between bending strength and electrical conductivity of CNT-dispersed Si<sub>3</sub>N<sub>4</sub> ceramics fired at 1600-1750°C (a) 1.0 wt% CNT addition, (b) 0.5 wt% CNT addition.

the electrical conductivity of CNT-dispersed Si<sub>3</sub>N<sub>4</sub> ceramics.

Fig. 5 shows the relationship between the electrical conductivity and the bending strength of the samples. Sample HT showed higher electrical conductivity and higher bending strength than sample T, because a larger amount of CNTs most likely remained in sample HT than in sample T. Consequently, we were able to achieve high bending strength and high electrical conductivity in the ceramics simultaneously.

### 4 Conclusions

In this study, CNT-dispersed Si<sub>3</sub>N<sub>4</sub> ceramics were fabricated using CNTs, which remained in the sintered body for a low GPS temperature. By using HfO<sub>2</sub> and TiO<sub>2</sub> as a sintering additive, we succeeded in fabricating dense CNT-dispersed Si<sub>3</sub>N<sub>4</sub> ceramics. The relative densities of all the specimens were very high, and they were above 93% after GPS and above 96% after HIP. Sample HT had high bending strength at a low GPS temperature. The bending strength values of sample HT fired at 1750°C were 985 MPa and 814 MPa for

0.5 and 1.0 wt% CNT addition, respectively. Sample HT showed higher electrical conductivity at a low GPS temperature. The electrical conductivity of sample HT, fabricated by adding 1.0 wt% of CNT and fired at 1750°C, was 51 S/m. This value was three times as high as that of sample T, fabricated by adding the same amount of CNTs and fired at 1700°C. HfO<sub>2</sub> and TiO<sub>2</sub> promoted the densification of Si<sub>3</sub>N<sub>4</sub> while improving the reaction resistance of the CNTs, thereby suppressing the reaction and disappearance of CNTs. The HfO<sub>2</sub> and TiO<sub>2</sub> additive and low temperature densification improved the bending strength and electrical conductivity of CNT-dispersed Si<sub>3</sub>N<sub>4</sub> ceramics. That is, we could achieve both high strength and high electrical conductivity by adding HfO<sub>2</sub> and TiO<sub>2</sub>.

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