Development of CNT-Si₃N₄ Composites with High Strength and Electrical Conductivity by Adding HfO₂

Mitsuaki Matsuoka, Sara Yoshio, Tomohiro Yamakawa, Junichi Tatami, Toru Wakihara, Katsutoshi Komeya and Takeshi Meguro

Graduate School of Environment and Information Sciences, Yokohama National University, Yokohama 240-8501, Japan

E-mail: tatami@ynu.ac.jp

The preparation of electrically conductive silicon nitride (Si₃N₄) ceramics by dispersing carbon nanotubes (CNTs) has been studied in the recent years. However, the density and strength of Si₃N₄ ceramics was found to deteriorate and the CNTs disappeared after firing at high temperatures because CNTs prevent Si₃N₄ from densification and there is a possibility that the CNTs reacted with the Si₃N₄ or SiO₂. To prevent the CNTs from reacting and disappearing, low temperature densification is required. In this study, HfO₂ was added to a Si₃N₄-Y₂O₃-Al₂O₃-AlN system to fabricate CNT-dispersed Si₃N₄ ceramics at low temperatures. As a result, a sample to which HfO₂ had been added and which was fired at lower temperatures showed higher electrical conductivity and higher bending strength. It was also observed that the mechanical and electrical properties of the ceramics depended on the quantity of added CNTs.

Key words: Silicon Nitride, Carbon Nanotube, Hafnium Oxide, Titanium Oxide, Electrical Conductivity

I. Introduction

Silicon nitride (Si₃N₄) 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. [1-3] Silicon nitride itself is an insulator, and hence, conventional Si₃N₄ ceramics are also insulators. Dust adheres easily onto the surface of such Si₃N₄ 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. [4-6] 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 Si₃N₄ ceramics, CNTs react with Si₃N₄ and SiO₂ at high temperatures to generate gases such as nitrogen, carbon monoxide, and carbon dioxide. The formation of these gases also suppresses the densification of Si₃N₄ ceramics, and the added CNTs disappear during the firing process. To prevent the CNTs from reacting and disappearing, densification needs to be carried out at a low temperature. In a previous study on CNT-dispersed Si₃N₄ ceramics, many researchers applied various sintering processes like spark plasma sintering and hot pressing to obtain dense ceramics. [7-9] Dense CNT-dispersed Si₃N₄ ceramics was fabricated using TiO₂ as a sintering aid in our previous study, [10-12] because TiO₂ improves densification of Si₃N₄. [13] In this study,

we focused on HfO₂ as a sintering aid because it promotes the densification of Si₃N₄ on account of the reaction between HfO₂, Y₂O₃, and Si₂O₃ at around 1600°C to generate a liquid phase. [14-15] HfO₂ should be able to prevent CNTs from disappearing because it reportedly prevents the oxidation of carbon and SiC. [16-17] Therefore, it is expected that as an additive, HfO₂ makes it possible for CNT-dispersed Si₃N₄ 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 HfO₂ as a sintering aid during fabrication on the electrical and mechanical properties of CNT-dispersed Si₃N₄ ceramics.

II. Experimental Procedure

Fine high-purity powders of Si₃N₄ (SN-E-10, Ube Industries, Ltd., Japan), Y₂O₃ (RU, Shin-Etsu Chemical Co., Ltd., Japan), Al₂O₃ (AKP-30, Sumitomo Chemical Co., Ltd., Japan), AlN (F grade, Tokuyama Co., Japan), HfO₂ (HFO01PB, Kojundo Chemical Laboratory Co., Ltd., Japan), and TiO₂ (R-11-P, Sakai Chemical Industry Co., Ltd., Japan), were used as raw materials. The multiwall carbon nanotubes used in this study (VGCFs, Showa Denko K.K., Japan) had diameters of 60 nm and lengths of 6 μm. Si₃N₄, Y₂O₃, Al₂O₃, AlN, HfO₂, and TiO₂ powders were weighed in the proportion 92:5:3:5:5, in that order. The samples containing HfO₂ and TiO₂ were labeled sample H 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 Si₃N₄, Y₂O₃, Al₂O₃, AlN, HfO₂ and TiO₂ 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 μm . 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 N_2 flow. After dewaxing, the green bodies were fired at 1600, 1650, 1700 and 1750°C for 2 h in 0.9 MPa 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 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.

III. Results and Discussion

Figure 1 shows the SEM image of the fracture surface of sample H containing 1.0 wt% of CNT and fired at 1600°C. The tuberos 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 Si_3N_4 ceramics developed in our previous research [10–12]. The CNTs dispersed well and existed randomly; thus, the formation of electrical conduction paths could be expected. Apparently, HfO_2 played an important role in causing CNTs to remain in the sintered body even after sintering.

Figure 2 shows the relative density of the sintered specimens. The relative densities of all the specimens were very high. They were above 90% after GPS and above 93% 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 research on CNT-disper-

Fig.1. SEM image of CNT-dispersed Si_3N_4 ceramics fired at 1600°C.

Fig.2. Relative density of CNT-dispersed Si_3N_4 ceramics fired at 1600–1750°C (a)GPS, (b)GPS+HIP.

sed Si_3N_4 ceramics [10–12]. The reason for the degradation of the density was that the CNTs hampered the densification of Si_3N_4 by forming gases after reacting with Si_3N_4 or SiO_2 .

Figure 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 Si_3N_4 or SiO_2 possibly suppress densification and large agglomerates of CNTs act as fracture origins. Samples H fired at 1700°C had bending strengths of 932 MPa and 834 MPa after the addition of 0.5 and 1.0 wt% CNT, respectively. These values were as high as the bending strength of sample H without the addition of CNTs. In particular, they were higher than those of sample T containing 0.5 wt% CNT and fired at 1600, 1650, and 1700°C.

Figure 4 shows the electrical conductivity of the sintered specimens. The electrical conductivity of sample H and sample T increased with an increase in the quantity of CNTs. The electrical conductivity of sample T increased with an increase in the GPS temperature for 1.0 wt% CNT addition. Sample T, with 0.5 wt% CNT addition, was an insulator, regardless of the GPS temperature. Sample H showed higher electrical conductivity than sample T. Although sample T, fabricated by adding 0.5 wt% CNT, was an insulator, sample H, fabricated by adding the same quantity of CNTs, showed electrical conductivity. The electrical conductivity of sample H, fabricated by adding 1.0 wt%

Fig.3. Bending strength of CNT-dispersed Si_3N_4 ceramics fired at 1600-1750°C (a) 5 wt% HfO_2 addition, (b) 5 wt% TiO_2 addition

Fig.4. Electrical conductivity of CNT- Si_3N_4 ceramics fired at 1600-1750°C

CNT and fired at 1600°C, was 59 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_2 improved the oxidation resistance of silicon carbide compositionally graded graphite. [16-17] In our study, sample H had higher electrical conductivity than sample T. This was probably a result of the prevention of the reaction of CNTs by HfO_2 , just as in the study conducted by Shimada. The HfO_2 additive improved the electrical conductivity of CNT-dispersed Si_3N_4 ceramics.

Figure 5 shows the relationship between the electrical

Fig.5. Relationship between relative density and electrical conductivity of CNT-dispersed Si_3N_4 ceramics fired at 1600-1750°C.

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

IV. Conclusions

In this study, CNT-dispersed Si_3N_4 ceramics were fabricated using CNTs, which remained in the sintered body for a low GPS temperature. By using HfO_2 as a sintering additive, we succeeded in fabricating dense CNT-dispersed Si_3N_4 ceramics. The relative densities of all the specimens were very high, and they were above 90% after GPS and above 93% after HIP. Sample H had high bending strength at a low temperature. The bending strength values of sample H fired at 1700°C were 932 MPa and 834 MPa for 0.5 and 1.0 wt% CNT addition, respectively. Sample H showed higher electrical conductivity at a low GPS temperature. The electrical conductivity of sample H, fabricated by adding 1.0 wt% of CNT and fired at 1600°C, was 59 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_2 promoted the densification of Si_3N_4 while improving the reaction resistance of the CNTs, thereby suppressing the reaction and disappearance of CNTs. The HfO_2 additive and low temperature densification improved the bending strength and electrical conductivity of CNT-dispersed Si_3N_4 ceramics. That is, we could achieve both high strength and high electrical conductivity by adding HfO_2 .

References

- [1] H. Kawamura and S. Yamamoto, SAE Paper, No. 830580 (1983).
- [2] Y. Tajima, Mater. Res. Soc. Symp. Proc., 287, 198-201 (1993).
- [3] K. Komeya and H. Kotani, JSAE Rev., 7, 72-79 (1986).
- [4] S. Iijima, Nature, 354, 56 (1991).
- [5] S. Rochie, Ann. Chim. Sci. Mater., 25, 529-532 (2000).

- [6] H. J. Dai, *Surf. Sci.*, 500, 218-241 (2002).
- [7] J. Dusza, G. Bluganb, J. Morgielc, J. Kueblerb, F. Inamd, T. Peijsd, M. J. Reeced and V. Puchya, *J. Eur. Ceram. Soc.*, 29, 3177-3184 (2009).
- [8] Cs. Balázs, Z. Shen, Z. Ko'nya, Zs. Kasztovszky, F. We'ber, Z. Ve'rtesy, L.P. Biro', I. Kiricsi and P. Arato, *Compos. Sci. Tech.*, 65, 727-733 (2004).
- [9] Cs. Balázs, F. S. Cinar, O. Addemir, F. Wéber and P. Arató, *J. Eur. Ceram. Soc.*, 24, 12, 3287-3294 (2004).
- [10] J. Tatami, T. Katashima, K. Komeya, T. Meguro and T. Wakihara, *J. Am. Ceram. Soc.*, 88, 2889-2893 (2005).
- [11] S. Yoshio, J. Tatami, T. Wakihara, K. Komeya and T. Meguro, *Key Eng. Mat.*, 403, 19-22 (2009).
- [12] S. Yoshio, J. Tatami, T. Wakihara, T. Yamakawa, H. Nakano, K. Komeya and T. Meguro, *J. Ceram. Soc. Japan*, 119 [1], 70-75 (2011).
- [13] J. Tatami, M. Toyama, K. Noguchi, K. Komeya, T. Meguro and M. Komatsu, *Key Eng. Mat.*, 247, 83-86 (2003).
- [14] H. Li, K. Komeya, J. Tatami, T. Meguro, Y. Chiba and M. Komatsu, *J. Ceram. Soc. Japan*, 109 [4], 342-346 (2001).
- [15] D. Horikawa, J. Tatami, T. Wakihara, K. Komeya and T. Meguro, *Key Eng. Mat.*, 403, 35-38 (2009).
- [16] S. Shimada and T. Sato, *Carbon*, 40 2469-2475 (2002).
- [17] S. Shimada and T. Aketo, *J. Am. Ceram. Soc.*, 88 [4], 845-849 (2005).

(Received April 29, 2011; Accepted July 6, 2011)