Effect of CNT quantity and sintering temperature on electrical and mechanical properties of CNT-dispersed Si$_3$N$_4$ ceramics

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Electrically conductive carbon nanotube (CNT)-dispersed ceramics with high strength were fabricated by varying the CNT quantity and the firing temperature. We investigated the effect of these factors on density, electrical conductivity, bending strength, and microstructure of the developed ceramics. The relative density of the CNT dispersed Si$_3$N$_4$ ceramics was higher than 90% except for the sample containing less than 1 wt % of CNTs and fired at a temperature of 1800°C. It was confirmed that CNTs exist in the samples with a higher density. The pullout length of CNTs on the fracture surface in samples fired at higher temperatures was shorter because of the degradation of the CNTs. By TEM observation, CNTs were found to exist in the grain boundary in the Si$_3$N$_4$ ceramics, and their diameter was found to be almost the same as that of raw CNTs. Electrical conductivity appeared in the samples by adding CNTs more than 1 wt % though the sample by adding 0.5 wt % CNTs was insulator. The electrical conductivities of the samples increased with an increase in the firing temperature, which was explained by the grain growth of β-Si$_3$N$_4$. The bending strength of the samples with 1 wt % of CNTs was as high as that of samples without CNTs. Thus, CNT-dispersed Si$_3$N$_4$ ceramics having both electrical conductivity and a higher bending strength were obtained by controlling the CNT quantity and the firing temperature.

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Key-words : Si$_3$N$_4$, CNT, Electrical conductivity, Strength, Gas pressure sintering, Sintering temperature

1. Introduction

Silicon nitride (Si$_3$N$_4$) has unique properties such as excellent hardness, high strength, high corrosion resistance, and high thermal conductivity. Because of these properties, Si$_3$N$_4$ ceramics have been used to fabricate structural components, cutting tools, and bearings.1–3 However, in some tribological applications, the system may break down because of the adhesion of fine particles or dust on the surface of the ceramics, which is caused by static electricity resulting from their high insulation. This problem can be solved by inducing electrical conduction through the Si$_3$N$_4$ ceramics. Some of the studies on electrically conductive Si$_3$N$_4$ ceramics have been carried out by using the ionic conductive glassy phase or by adding the conductive particles such as TiN or SiC. The mechanical properties of these Si$_3$N$_4$ ceramics are insufficient for structural applications.3,5,6

Carbon nanotubes (CNTs) have been used as fillers with electrical conductivity, high elastic modulus, high strength, and high aspect ratio.6–10 In particular, CNTs have unusual dimensions a nanometer diameter and a high aspect ratio resulting in a low percolation threshold for electrical conductivity. Most previous studies on CNT-dispersed Si$_3$N$_4$ ceramics focused on their mechanical properties and only a few papers reported their electrical conductivity.8,10 We succeeded in the fabrication of electrically conductive CNT-dispersed Si$_3$N$_4$ ceramics using sintering aids for low-temperature densification.11 We also reported the influence of the geometry of CNTs on their density and electrical conductivity.12,13 However, the effect of the CNT quantity, especially close to the percolation threshold, on density, electrical conductivity, and mechanical properties is not yet known. The sintering temperature also affects the densification of Si$_3$N$_4$ and the reaction between CNT and Si$_3$N$_4$ or SiO$_2$. In this study, we fabricated CNT-dispersed Si$_3$N$_4$ ceramics by changing the CNT quantity and the sintering temperature. We evaluated density, electrical conductivity, mechanical properties, and microstructure of the resulting CNT-dispersed Si$_3$N$_4$ ceramics.

2. Experimental procedure

Fine high-purity powders of Si$_3$N$_4$ (SN-E-10, Ube Co. Ltd., Japan), Y$_2$O$_3$ (RU, Shinetu Chemical Co.), Al$_2$O$_3$ (AKP-30, Sumitomo Chemical Co., Japan), AIN (F grade, Tokuyama Co., Japan), and TiO$_2$ (R-11-P, Sakai Chemical Co., Japan) were used as raw materials. The multiwall carbon nanotubes used in this study (VGCFs, Showa Denko Co., Japan) had diameters of 60 nm and lengths of 6 μm. The batch compositions of the samples are listed in Table 1. CNTs and a dispersant (Seruna E503, Chukyoyushi Co., Japan) were added to ethanol. After ultrasonication for 20 min, the Si$_3$N$_4$, Y$_2$O$_3$, Al$_2$O$_3$, AIN, and TiO$_2$ powders were added to the CNT slurry with 2 wt% of the dispersant (Seruna E503, Chukyoyushi Co.). Ball milling was carried out at 110 rpm for 48 h using 5-mm sialon balls to mix the powders. The weight ratio of the balls to the powder was 4.65.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Si$_3$N$_4$</th>
<th>Y$_2$O$_3$</th>
<th>Al$_2$O$_3$</th>
<th>AIN</th>
<th>TiO$_2$</th>
<th>CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>92</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>92</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>92</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 1. Batch composition for CNT-dispersed Si$_3$N$_4$ ceramics

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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 Junyaku Co., Japan) were added as the binder and lubricant, respectively, to make granules by sieving the mixed powder using a nylon mesh with openings of 250 μm. The granules were molded into 35 × 45 × 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 4 L/min N2 flow. After dewaxing, the green bodies were fired at 1700, 1750, and 1800°C for 2 h in 0.9 MPa N2 using a gas pressure sintering (GPS) furnace (Himult 5000, Fujidenpa Kogyo Co., Japan). For more densification, the gas pressure sintered samples were densified by a hot isostatic pressing (HIP) at 1700°C for 1 h under 100 MPa N2.

The density of the samples was measured by the Archimedes method. The carbon content was measured by the infrared absorbance technique (EGMA-650, HORIBA Co., Japan). The phase was identified by the X-ray diffraction method (Multiflex, Rigaku Co., Japan). The microstructure was observed using a scanning electron microscope (JSM-5200, JEOL, Japan). The CNTs were characterized by Raman spectrometry (in Via, Renishow PLC., England). The electrical conductivity was measured by the four-terminal method. The bending strength was measured by performing a three-point bending test with a span of 30 mm.

### 3. Results and discussion

Table 2 shows the relative density and the amount of carbon in the sintered body. Si₃N₄ ceramics without CNTs having the same sintering aids used in this study were densified over 1600°C firing in our previous study. The former density of Si₃N₄ ceramics with CNTs after GPS was higher than 90% except for the samples of composition A and B fired at 1800°C. The relative density slightly increased after HIPping and the tendency of the relative density after HIPping was the same as that after GPS. The relative densities of the samples fired at 1700 and 1750°C were higher than that of the sample fired at 1800°C. The former densities were independent of the CNT quantity whereas that of the sample fired at 1800°C increased with a decrease in the CNT quantity. In the samples fired at 1700 and 1750°C the carbon is as much as 70% of the added CNTs. On the other hand, the fraction of residual carbon in the sample fired at 1800°C decreases with a decrease in the added CNTs.

As shown in Fig. 1, the samples of composition A and B fired at 1800°C swelled up in the center of the plate. According to thermodynamics, the following reactions with gas formation can occur during firing at high temperatures.

![Fig. 1.](image)

These reactions become more marked at higher firing temperatures. Taking account of the lack of swelling in the samples fired below 1750°C, the above reactions were remarkably advanced around 1800°C in the Si₃N₄ ceramics. Meanwhile, the sample of composition C did not swell even when fired at 1800°C; in this sample the relative density is 94.6% and the residual carbon was 78% of the added CNTs. For CNT-ZrO₂ composites, it is reported that the reduction in the grain-boundary sliding caused by the addition of CNTs improves the creep resistance at high temperatures. The high-temperature deformation of Si₃N₄ ceramics mainly results from the grain-boundary sliding, due to the grain-boundary glassy phase. Although the high-temperature deformation behavior of the sample used in this study has not been studied yet, the swelling of the sample due to gas formation was probably restrained because the CNT dispersion improved the creep resistance.

### Table 2. Characteristics of CNT-dispersed Si₃N₄ ceramics fabricated by various compositions and GPS temperatures

<table>
<thead>
<tr>
<th>Composition</th>
<th>GPS temperature (°C)</th>
<th>Relative density after GPS (%)</th>
<th>Relative density after HIP (%)</th>
<th>Amount of carbon (%)</th>
<th>Residual carbon rate (%)</th>
<th>Electrical conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1700</td>
<td>97.4</td>
<td>98.5</td>
<td>0.41</td>
<td>81</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>1700</td>
<td>96.0</td>
<td>98.8</td>
<td>0.54</td>
<td>54</td>
<td>17</td>
</tr>
<tr>
<td>C</td>
<td>1700</td>
<td>92.1</td>
<td>96.6</td>
<td>1.40</td>
<td>79</td>
<td>83</td>
</tr>
<tr>
<td>A</td>
<td>1750</td>
<td>96.4</td>
<td>98.5</td>
<td>0.32</td>
<td>63</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>1750</td>
<td>95.2</td>
<td>98.6</td>
<td>0.76</td>
<td>76</td>
<td>28</td>
</tr>
<tr>
<td>C</td>
<td>1750</td>
<td>93.2</td>
<td>98.6</td>
<td>1.42</td>
<td>79</td>
<td>86</td>
</tr>
<tr>
<td>A</td>
<td>1800</td>
<td>82.2</td>
<td>83.6</td>
<td>0.20</td>
<td>40</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>1800</td>
<td>83.2</td>
<td>87.2</td>
<td>0.62</td>
<td>62</td>
<td>62</td>
</tr>
<tr>
<td>C</td>
<td>1800</td>
<td>92.0</td>
<td>84.6</td>
<td>1.39</td>
<td>78</td>
<td>110</td>
</tr>
<tr>
<td>Without CNT</td>
<td>1700</td>
<td>97.9</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Without CNT</td>
<td>1800</td>
<td>98.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
study,\(^{13}\) which means that the \(\alpha\rightarrow\beta\) phase transformation was complete and this transformation enhanced the densification of Si\(_3\)N\(_4\). TiN was generated by the reaction of TiO\(_2\) with Si\(_3\)N\(_4\) or AlN.\(^{13,15}\) Tatami et al. have reported that C, in the form of carbon nanotubes, reacts with SiO\(_2\) or Si\(_3\)N\(_4\) to form SiC because CNTs disappear when the CNT quantity is too large or the sintering aids are not appropriate.\(^{11}\) In this study, a small quantity of the added CNTs disappeared, as shown in Table 2. Although it is difficult to discuss the actual reaction at high temperature because no information about partial pressure of CO and SiO near the sintered body at high temperatures, it was expected that reaction (1) predominantly occurred judging from the XRD profile. There is a possibility of the formation of SiC, but the XRD peak for SiC did not appear, indicating that a negligible amount of SiC was formed in the firing process.

Figure 3 shows SEM images of the fracture surfaces of the developed CNT-dispersed Si\(_3\)N\(_4\) ceramics. CNTs were confirmed to exist in all the samples except for compositions A and B fired at 1800° C; the residual carbon was regarded as the quantity of the residual CNTs except for the swelled sample. The CNT quantity observed increased with an increase in the added CNTs. In the samples of composition A and B fired at 1800° C that swelled after GPS, it was found that there were many large pores in the sintered body due to gas formation by the reaction between CNT and SiO\(_2\) or Si\(_3\)N\(_4\). The sample of composition C fired at a lower temperature showed a longer pullout length of CNTs although the amount of residual carbon was independent of the firing temperature. The pullout length of CNTs in the fracture surface depends on the strength of the CNTs, the thermal residual stress, and the interfacial strength between the CNTs and Si\(_3\)N\(_4\), which
results from the analogy with fiber-reinforced composites. Given that higher-temperature firing led to a shorter pullout length, the following phenomena should occur in higher-temperature firing: strength degradation of CNTs because of the formation of defects; larger residual stress because of a thermal expansion mismatch between the CNTs and Si$_3$N$_4$; and higher interfacial strength because of the formation of an interfacial layer.

To examine the defects and residual stress of the CNTs, Raman spectra were measured. Figure 4 shows the Raman spectra of the sample of composition C. Both G band and D band were observed, and this is the typical pattern of MWCNT. G band corresponds to in-plane stretching vibration and D band originates from the disordered or defect mode. The peak positions of the D and G bands were 1352 and 1583 cm$^{-1}$, respectively, which is slightly lower than the value for raw CNTs and independent of the firing temperature. It is known that the peak of the G and D bands shift depending on the stress applied to the CNTs. There was no change in the peak positions of the D and G bands in spite of different temperatures. This means that the thermal residual stress in the CNTs was almost the same in all the samples used in this study. However, it is understood that thermal residual stress is generated from the slight shift in the peak compared with that for raw CNTs. On the other hand, the ratio of the areas of the G and D bands (G/D ratio) depends on the firing temperature: 10.9 at 1700°C, 7.2 at 1750°C, and 6.0 at 1800°C. In consideration of the origin of the D band, the defects in the CNTs increased with an increase in the firing temperature. It has been reported that the strength of CNTs decreased and the interfacial strength with the matrix increased with an increase in the CNT defects. As a result, the shorter pullout length of the CNTs resulted in the formation of defects in the CNTs after heat treatment.

Figure 5 shows TEM images of CNT-dispersed Si$_3$N$_4$. The arrows in Fig. 5(a) indicate CNTs. CNTs were observed in the grain boundary in the Si$_3$N$_4$ ceramics. The size of the CNTs was almost the same as that of raw CNTs. Figure 5(b) is an enlarged view of a CNT. The layered structure peculiar to CNTs was confirmed. A reaction phase was not observed in the interfaces between CNTs and Si$_3$N$_4$ or the grain-boundary glassy phase, which corresponded to SiC missing from the XRD analysis.

The electrical conductivity of CNT-dispersed Si$_3$N$_4$ ceramics is listed in Table 2; it was measured using only the high-density samples. The samples of composition B and C showed electrical conductivity, but composition A was an insulator in the same way as conventional Si$_3$N$_4$ ceramics without CNTs. Electrical conductivity due to the dispersion of conductive particles generally appears when the quantity of the particles is more than a critical value, namely the percolation threshold. Composition A did not indicate electrical conductivity because the CNT quantity is lower than the percolation threshold for electrical conductivity. The electrical conductivities of the samples of composition C fired at 1700°C and 1750°C were 83 and 86 S/m respectively, higher than those of composition B. The difference in the electrical conductivity is because of the difference in the CNT quantity. Furthermore, the electrical conductivity increased with an increase in the firing temperature and was 110 S/m in the sample of composition C fired at 1800°C. In composition C, the amount of carbon in the sample was independent of the firing temperature, which means that the CNT quantity should remain constant. Since the Si$_3$N$_4$ grains grew with an increase in the firing temperature, as shown in Fig. 6, it is possible that the microstructure of the Si$_3$N$_4$ ceramics affects the electrical conductivity. The CNTs are probably concentrated in the grain boundary with grain growth because grain growth leads to a decrease in the area of the grain boundary, and the CNTs were dispersed in the grain boundary as shown in Fig. 5. The electrical conductivity depends on the CNT concentration. The grain size

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**Fig. 4.** Raman spectra of raw CNTs and CNT-dispersed Si$_3$N$_4$ ceramics of composition C fired at various temperatures.

![Raman spectra](image)

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**Fig. 5.** TEM photographs of CNT-dispersed Si$_3$N$_4$ ceramics of composition C, fired at 1750°C. (b) and (c) are enlarged views of position 1 in (a). (d) and (e) are enlarged views of position 2 in (a).
of $\beta$-Si$_3$N$_4$, measured by the linear intercept method using the SEM photographs in Fig. 6, varied from 310 to 500 nm with increasing firing temperature. The relationship between the grain size and the electrical conductivity of composition C is plotted in Fig. 7. The electrical conductivity increased with increase in the grain size. This is probably because the area of the grain boundary per unit volume decreases with increasing the grain size and the electrical conductivity increases with decreasing area of the grain boundary. In the future work, the electrical conductivity of the CNT-dispersed Si$_3$N$_4$ ceramics will be discussed based on the new percolation theory in consideration of the microstructure of matrix Si$_3$N$_4$ ceramics.

Table 3 shows the bending strength of CNT-dispersed Si$_3$N$_4$ ceramics. The bending strength of the sample of composition C with a higher CNT quantity was about 500 MPa, lower than the value for Si$_3$N$_4$ ceramics without CNTs. As a result of the fractography the fracture origin was an agglomeration of CNTs. On the other hand, the bending strength of composition B was higher than that of composition C and the same or higher than that of Si$_3$N$_4$ ceramics without CNTs. Thus, CNT-dispersed Si$_3$N$_4$ ceramics with electrical conductivity and a higher bending strength can be achieved by controlling the CNT quantity and the firing temperature. The bending strength strongly depends on the size and quantity of fracture origins. The reason for the higher strength in composition B seems to be that the fracture origins due to the agglomeration of CNTs were fewer than those for composition C. If the bending test is carried out using more specimens (we performed five bending tests for each sample) or by a four-point bending test with a large effective volume, there is a possibility of fractures that are a result of the agglomeration of CNTs like composition C. To make more reliable CNT-dispersed Si$_3$N$_4$ ceramics, future work will investigate the uniform dispersion of the CNTs.

![Fig. 6. SEM images of plasma etched surfaces of CNT-dispersed Si$_3$N$_4$ ceramics of Composition C fired at (a) 1700, (b) 1750 and (c) 1800°C.](image)

![Fig. 7. Relationship between the grain size and the electrical conductivity of CNT-dispersed Si$_3$N$_4$ ceramics of composition C.](image)

**Table 3. Bending strength of CNT-dispersed Si$_3$N$_4$ ceramics**

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Composition B</th>
<th>Composition C</th>
<th>Without CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1700</td>
<td>732</td>
<td>998</td>
<td>929</td>
</tr>
<tr>
<td>1750</td>
<td>732</td>
<td>998</td>
<td>929</td>
</tr>
<tr>
<td>1800</td>
<td>863</td>
<td>513</td>
<td>950</td>
</tr>
</tbody>
</table>

### 4. Conclusions

In this study, CNT-dispersed Si$_3$N$_4$ ceramics are prepared for different CNT quantity and sintering temperatures were fabricated. The relative densities of the samples fired at 1700 and 1750°C were higher than that of the samples fired at 1800°C. The former densities were independent of the CNT quantity whereas that of the sample fired at 1800°C decreased with a decrease in the CNT quantity. In the samples fired at 1700 and 1750°C, the fraction of carbon in the added CNTs is as much as 70%. On the other hand, the fraction of residual carbon in the sample fired at 1800°C decreases with a decrease in the CNT quantity. CNTs were confirmed to exist in all the samples except for composition A and B fired at 1800°C. The observed CNT quantity increased with an increase in the added CNTs. The sample fired at a lower temperature showed CNTs with longer pullout lengths although the amount of residual carbon was independent of the firing temperature. It was shown that the shorter pullout length of CNTs resulted in the formation of defects in the CNTs after heat treatment. The samples by adding 1.0 wt% CNT showed electrical conductivity, but the samples by adding 0.5 wt% CNT was an insulator. The electrical conductivities of the samples by adding 1.8 wt% CNT fired at 1700 and 1750°C were 83 and 86 S/m, respectively. The electrical conductivity also increased with an increase in the firing temperature, which was explained by grain growth of $\beta$-Si$_3$N$_4$. The bending strength of the sample by adding 1.0 wt% CNT was the same or higher than that of Si$_3$N$_4$ ceramics with CNT quantity was about 500 MPa, which is lower than the value for the without CNTs. Consequently, CNT-dispersed Si$_3$N$_4$ ceramics with electrical conductivity and a higher bending strength can be achieved by controlling the CNT quantity and the firing temperature.

### References