Densification and Mechanical Properties of Electroconductive Si₃N₄-Based Composites Prepared by Spark Plasma Sintering

(Norhayati Ahmad* & Hidekazu Sueyoshi)

ABSTRACT

Si₃N₄-TiN composites were prepared by conventional powder processing (SPS1) and in-situ reaction sintering (SPS2). Rapid densification of SPS was achieved for sample SPS1 and SPS2 within a few minutes at low temperature. Sample SPS1 sintered at 1550°C showed rapid transformation of α to β Si₃N₄ while for sample SPS2 sintered at 1350°C, a significant degree of α to β Si₃N₄ transformation was achieved. Homogeneous distribution of equiaxed TiN grains in matrix Si₃N₄ resulting in high hardness (21.7 GPa) and bending strength (621 MPa) for sample SPS1 sintered at 1550°C. Elongated TiN grains as the reinforcement of Si₃N₄ matrix composites was found to increase the toughness (8.39 MPa m⁰.⁵) of sample SPS2 sintered at 1350°C. The composites prepared by SPS2 sintered at 1250-1350°C low had electrical resistivity and could be machined by electrical discharge machining (EDM).

Keywords: Densification; mechanical properties; silicon nitride-titanium nitride composites; spark plasma sintering

INTRODUCTION

Si₃N₄-based ceramics are promising materials for applications in gas turbine components, heat exchangers and wear-resistant components. Most of these applications require good strength and toughness, high thermal conductivity and good environmental stability at high temperature. Furthermore, Si₃N₄ components must be machined by using diamond tool, due to their low electrical conductivity. Diamond machining is a costly process, which also implies limitations on the complexity of the final shapes. The addition of electroconductive phases to insulating ceramics in suitable amounts is a straightforward strategy to overcome this problem, since it allows components to be machined by electro-discharge machining (EDM) (Bellosi et al. 1992; Liu & Huang 2003). All these considerations have led to the attempt to fabricate electroconductive Si₃N₄-based materials with improved mechanical properties. For this aim, the Si₃N₄ matrix was simultaneously added with TiN particles. TiN has been coupled to several ceramic matrixes, such as Si₃N₄, Al₂O₃, ZrO₂ and it has been found that TiN addition causes a significant improvement in the mechanical properties (Bellosi et al. 1992; Liu & Huang 2003; Salehi et al. 2006; Wang et al. 2006) and the oxidation resistance (Mazerolles et al. 2005).

Recent development of novel sintering techniques enables us not only to produce dense solids, but also to control their microstructure and mechanical properties. Spark plasma sintering (SPS) is similar to hot-pressing to the extent that graphite dies are used, but the heating is accomplished by spark discharges in voids between the particles, generated by an instantaneous pulsed direct current which is applied through electrodes at the top and bottom punches of the graphite die. Due to these discharges, the particle surface is activated and purified, and a self-heating phenomenon is generated between the particles, as a result of which heat-transfer and mass-transfer can be completed instantaneously (Gao & Miyamoto 1997; Gao et al. 1998; Parera et al. 1998; Tokita 1993). Many investigations have been performed concerning the densification mechanism of Si₃N₄-based ceramics by rapid sintering process. It is said that the sintering...
proceeds very quickly mainly because of the spark plasma caused by the large pulse current, thus allowing nanosized grains of the starting powder and its crystal structure as well, to be retained in the sintered body. Generally, the Kingery sintering model has been used in describing the densification results (Bowen et al. 1978; Lewis 1980; Messier et al. 1978). Today, most Si$_3$N$_4$ ceramics are prepared by using α-rich Si$_3$N$_4$ powders, which transform during sintering into β-Si$_3$N$_4$. The β-modification forms elongated needle-like grains with high aspect ratios. This can be attributed to the relatively complex microstructure developed during densification by liquid phase sintering (Weiss & Kaysser 1978).

The objective of this work was to compare the sinterability, the microstructure and the mechanical properties of Si$_3$N$_4$ – TiN composites prepared by conventional sintering of a mixture of Si$_3$N$_4$ and TiN powders and in-situ reaction sintering of Si$_3$N$_4$ and Ti powders. By using a novel rapid sintering method, SPS has been applied to sinter a composite at different temperatures. The samples obtained by SPS have advantages such as a more homogeneous microstructure, a higher density and excellent mechanical properties.

**EXPERIMENTAL METHODS**

The basic raw material used for preparing the composites was nanosized Si$_3$N$_4$ powder containing 5 mass % Y$_2$O$_3$ and 2 mass % Al$_2$O$_3$ as sintering additive (Wako Co. Ltd., mean particle size 60 nm). The Si$_3$N$_4$ powder was mixed with TiN powder (Wako Co. Ltd., mean particle size 50 nm) and Ti powder (Wako Co. Ltd., mean particle size 45 μm) for sample SPS1 and SPS2, respectively. The composition of starting powder mixtures and some details about preparation methods used in experiments are shown in Table 1.

The powders measured according to Table 1 were mixed by planetary ball milling (Pulverisette 6, Fritsch Co. Ltd.) in ethanol. After drying, the mixed powders were screened and enclosed in a graphite die, then were sintered by SPS-3.20 MK-4 (Sumitomo Coal Co. Ltd.). During heating, the change in thickness of the specimen was measured by a dilatometer to monitor the densification behaviour. Sintered disks obtained by SPS were 15 mm in diameter. Density measurements were made using the Archimedes technique with an immersion medium of distilled water. The crystalline structure was examined by X-ray diffraction (XRD-6000S, Shimadzu Co. Ltd.), which was performed with CuK$_\alpha$ radiation at a scanning rate of 3°/min. By comparing the peak intensity in the XRD patterns, the α/β - Si$_3$N$_4$ ratios were calculated based on measurements of the ratio of intensities of the α$_{200}$ and β$_{200}$ reflections (Kall 1988). All the resulting disks were cut and ground into bars (3 x 4 x 15 mm$^3$) for strength measurements. The strength was measured with a mechanical machine (AG-1, Shimadzu Co. Ltd.) using three-point bending test with a span length of 10 mm and a crosshead speed of 0.1 mm/min. Fracture surfaces were examined by scanning electron microscopy (ESEM XL-30 Series, Philips Co. Ltd.). Hardness was obtained by Vickers microhardness (HMV, Shimadzu Co. Ltd.) with an indentation load of 19.614 N for 30 s. The fracture toughness was measured by indentation method and calculated according to the equation given by Niihara et al. (1982). The electrical resistivity was measured at room temperature on the polished surface of the specimen (2 x 3 x 14 mm$^3$) using the four-point probe method. The machinability of the composites was examined by EDM (Robocut α-OA, Fanuc Co. Ltd.) with 0.25 mm diameter of Cu wire at a speed of 0.2 mm/min.

**RESULTS AND DISCUSSION**

Typical shrinkage data (ΔL/L) recorded during sintering of SPS1 and SPS2 versus time are shown in Figures 1 and 2, respectively. The shrinkage curves recorded for sample SPS1 sintered at 1550 and 1600°C showed a narrow time interval ranging from ~18 min to ~23.5 min which densify in a very short time (~5.5 min) compared with sample sintered at 1450 and 1500°C (~11 min). Sample SPS2 sintered at 1300 and 1350°C showed rapid densifications (~8.5 min) as compared with sample sintered at 1200 and 1250°C (~11 min). Rapid densification of SPS was achieved for sample SPS1 and SPS2 within a few minutes. In conventional hot pressing, the densification of Si$_3$N$_4$-based ceramics takes several hours and the densification is accompanied by phase transformations/reactions and grain growth. Using SPS, however, the densification of Si$_3$N$_4$-TiN composites can be accomplished by sintering for short holding time at low temperature.

**TABLE 1. Starting compositions and preparation conditions of Si$_3$N$_4$-TiN composites**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Starting powders (mass %)</th>
<th>Ball milling parameter</th>
<th>Sintering parameter</th>
<th>Holding time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si$_3$N$_4$</td>
<td>TiN</td>
<td>Ti</td>
<td>Time (h)</td>
</tr>
<tr>
<td>SPS1</td>
<td>70</td>
<td>30</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>SPS2</td>
<td>70</td>
<td>-</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>
TABLE 2. Density (ρ), crystalline phase (β-Si₃N₄), Vickers microhardness (Hv), bending strength (σ), fracture toughness (KIC) and electrical resistivity of composites at different temperatures

<table>
<thead>
<tr>
<th>Samples</th>
<th>T (ºC)</th>
<th>ρ (g/cm³)</th>
<th>β-Si₃N₄ (%)</th>
<th>Hv (GPa)</th>
<th>σ(MPa)</th>
<th>KIC (MPa m¹/₂)</th>
<th>Electrical resistivity (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPS1</td>
<td>1450</td>
<td>3.13</td>
<td>66.6</td>
<td>7.61</td>
<td>183</td>
<td>2.67</td>
<td>5x10¹³</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>3.47</td>
<td>87.7</td>
<td>19.53</td>
<td>547</td>
<td>3.10</td>
<td>8.73 x 10⁴</td>
</tr>
<tr>
<td></td>
<td>1550</td>
<td>3.65</td>
<td>90.8</td>
<td>21.71</td>
<td>621</td>
<td>4.16</td>
<td>6.14 x 10²</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>3.65</td>
<td>91.6</td>
<td>18.99</td>
<td>569</td>
<td>3.36</td>
<td>3.46</td>
</tr>
<tr>
<td>SPS2</td>
<td>1200</td>
<td>2.69</td>
<td>47.1</td>
<td>5.48</td>
<td>155</td>
<td>1.72</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>3.03</td>
<td>49.2</td>
<td>7.56</td>
<td>198</td>
<td>3.24</td>
<td>6.30 x 10²</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>3.24</td>
<td>51.5</td>
<td>17.78</td>
<td>355</td>
<td>8.39</td>
<td>1.33 x 10³</td>
</tr>
<tr>
<td></td>
<td>1350</td>
<td>3.41</td>
<td>58.5</td>
<td>19.95</td>
<td>328</td>
<td>6.56</td>
<td>4.29 x 10⁴</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>3.30</td>
<td>98.3</td>
<td>17.96</td>
<td>292</td>
<td>4.64</td>
<td>1.82 x 10²</td>
</tr>
<tr>
<td></td>
<td>1550</td>
<td>3.29</td>
<td>100.0</td>
<td>17.34</td>
<td>262</td>
<td>4.39</td>
<td>1.40 x 10³</td>
</tr>
</tbody>
</table>

As discussed in previous work (Norhayati Ahmad et al. 2009) the logarithm of shrinkage (ln \(\Delta L/L_o\)) was plotted versus logarithm of isothermal holding time (ln \(t\)) in order to determine the densification mechanism at early stage of sintering. The dominant mechanisms of sample SPS1 at 1450 and 1500ºC were a hybrid of dissolution-reprecipitation and viscous flow and at 1600ºC, the dominant mechanism was viscous flow. The dissolution of precipitate Si₃N₄ grains at early-formed oxygen-rich liquid is restricted below a certain critical temperature (1500ºC) and above this temperature, e.g. 1600ºC, the viscous flow is the dominant mechanisms because the dissolution process takes place rapidly and large amount of nitrogen-containing liquid is formed. The dominant mechanism for sample SPS2 at 1200 - 1300ºC was a hybrid of dissolution-reprecipitation and viscous flow (Norhayati Ahmad & Sueyoshi 2010, 2011). The synthesis of TiN by reaction sintering was promoted by dissolution-reprecipitation and viscous flow during SPS. The precipitate of small nodular β-Si₃N₄ initiated the solution of Si₃N₄ at contact point between particles and transported from small to large grain by diffusion. This nodular reacted with TiO₂ (from the surface of Ti powder) and Ti to form TiN. The large TiN grains grow at the expense of the small β-Si₃N₄ during the liquid-phase sintering. The formation of TiN along the nodular β-Si₃N₄ could be densified more quickly because of the rapid sintering rate in SPS.

β-Si₃N₄ content at different temperatures for sample SPS1 and SPS2 is shown in Table 2. The formation of β-Si₃N₄ is almost completed (90.8%) at 1550ºC for sample SPS1, while the transformation from α to β-Si₃N₄ is not completed (58.5%) at 1350ºC for sample SPS2. Therefore, for sample SPS1, the phase transformation happens and almost completes at a lower temperature with almost β-Si₃N₄ could be obtained at higher sintering temperature. On the other hand, a small degree of phase transformation of sample SPS2 occurs at lower temperature. Afterwards, sintering at higher temperature will cause further phase transformation that leads to rapid grain growth. Phase transformation and synthesis of Si₃N₄-based composite of sample SPS2 at lower temperature compared with sample SPS1 because liquid phase may spread around the Si₃N₄ particles due to pressure.
The BSE images of sample SPS1 sintered at 1600°C and SPS2 sintered at 1300°C are shown in Figure 3. The grey and white contrast phases are respectively the Si₃N₄ and TiN phase which was identified by EDX analysis. A homogeneous distribution of TiN particles was achieved by SPS at 1600°C (Figure 3(a)). Elongated TiN grains observed in sample SPS2 (Figure 3(b)) clearly indicates the formation of in-situ TiN grains during sintering.

The formations of equiaxed TiN grains for sample SPS1 are uniformly distributed in the Si₃N₄ matrix which contained fine-grained β-Si₃N₄ phase which resulted in high strength and hardness (Table 2). The nucleation and growth of TiN and silicon nitride grains occurred at the same time in this composite. For sample SPS2, the phase transformation and grain growth progresses so fast to develop into microstructures consisting of elongated TiN needles reinforced in the fine grains matrix Si₃N₄ with improved fracture toughness (Table 2). However, the presence of too large elongated TiN grains at higher temperature will deteriorated the fracture toughness. As shown in Table 2, the electrical resistivity of sample SPS2 sintered at 1250 - 1350°C (6.30 × 10⁻¹ – 4.29 × 10⁻¹ Ω cm) are enough to be EDM is machinable. This can be explained by the increased connectivity of elongated TiN grains in sample SPS2 as shown in Figure 3(b).

CONCLUSION
Almost all α-Si₃N₄ transform to β-Si₃N₄ for sample SPS1 sintered at 1550°C. For sample SPS2 sintered at 1300°C the reaction can be accomplished with very limited involvement of phase transformation. Therefore, the phase transformation sequence can be precisely followed and manipulated during further annealing after complete densification. The use of local thermal difference generated by the SPS under rapid heating and a short holding time appears to be a very effective way for producing well dispersed equiaxed TiN (sample SPS1) and elongated TiN (SPS2) which has been suggested to enhance the mechanical and electrical properties.

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REFERENCES

FIGURE 3. BSE images of polished surfaces for sample (a) SPS 1 and (b) SPS 2


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