Abstract

Dense silicon nitride (Si₃N₄) composites containing 1 wt% of multi-wall carbon nanotubes were prepared by spark plasma sintering (SPS), showing a quite homogeneous dispersion of the nanotubes into the matrix without signs of degradation. Peak temperature, holding time, applied pressure and vacuum level were modified to analyze their effect on the microstructure of the materials. The composite sintered at 1500 ºC had an 80 vol% α-Si₃N₄ phase without almost grain growth and showed the highest hardness (~ 18 GPa) but the lowest fracture toughness (4.4 MPa·m½) values. An increase of 50 ºC in the sintering temperature activated the α → β-Si₃N₄ phase transformation (60 vol % of β-phase) decreasing the hardness. The grain growth was promoted increasing the holding time at a given temperature, which caused higher fracture toughness due to the development of in-situ toughening mechanisms. MWNTs contributed to this toughening by the development of crack bridging effects.

1. Introduction

In the last few years, carbon nanotubes (CNTs) have raised expectation as reinforcing nanofibres for ceramic matrices, due to their excellent thermo-mechanical properties [1]. The first type of these new ceramic matrix composites (CMCs) was alumina-based, which allowed the use of low sintering temperatures (below 1300 ºC) preserving the integrity of the CNTs [2].

Non-oxide ceramics, such as silicon nitride (Si₃N₄), are widely used in technological applications under strong demanding conditions where good thermo-mechanical and tribological properties are required. In this sense, the performance of Si₃N₄-based materials in wear applications can be enhanced by adding CNTs due to their carbon-based composition that would promote the development of self-lubricating composites. However, high temperatures (1700-1800 ºC) are commonly required for sintering Si₃N₄ materials using conventional techniques, which produce the nanotubes degradation [3].

During the last decade, a new technique known as spark plasma sintering (SPS), based on a pressure assisted pulsed direct current sintering process, has allowed very fast heating rates and lower sintering temperatures [4], favouring both the manufacture of fully dense materials with constrained grain growth and the preservation of CNTs [5]. In the present work, Si₃N₄ composites with 1 wt% of multi-wall carbon nanotubes (MWNTs) were fabricated by the SPS technique. The influence of the SPS parameters on the microstructure and mechanical properties of the composites was also analyzed.

2. Experimental procedure

The as-received MWNTs, produced by supported catalyst chemical vapor deposition method [6], were aggregated into bundled networks of ropes due to van der Walls’ attraction (Fig. 1a). Therefore, MWNTs were dispersed in an aqueous solution containing a 0.05 wt% of a water soluble polysaccharide (Gum Arabic) within an ultrasonic bath for 210 min. Then, the solution was freeze-dried to remove the water and the polysaccharide was burned out at 300 ºC, leaving the MWNTs separated as shown in Fig. 1b.

Powder mixtures containing α-Si₃N₄ powders, sintering additives (5 wt% of Y₂O₃ and 4 wt% of Al₂O₃) and 1 wt% of the dispersed MWNTs were homogenised by ball milling for 2h in ethanol media. Afterwards, the slurry was dried using a rotary-evaporator and sieved through a 63 µm mesh. Disc-shaped specimens were obtained by SPS (DR. SINTER, Spark Plasma Sintering System, Syntex,
Manuel Belmonte, P. Miranzo, M.I. Osendi

Japan). Five different conditions were selected to analyze the effect of the SPS parameters on the microstructure of the specimens. Peak temperature, holding time, applied pressure, and vacuum level were varied in the ranges indicated in Table I, keeping constant the heating rate at ~ 100 °C•min⁻¹.

Table I. Spark plasma sintering conditions for the different materials.

<table>
<thead>
<tr>
<th>Sample ID</th>
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</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>1500</td>
<td>1550</td>
<td>1550</td>
<td>1550</td>
<td>1550</td>
</tr>
<tr>
<td>Holding time (min)</td>
<td>8</td>
<td>5</td>
<td>15</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td>80</td>
<td>50</td>
<td>50</td>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>Vacuum level (Pa)</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>300</td>
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</tbody>
</table>

Figure 1. SEM views of the as-received MWNTs (a) and after the dispersing treatment (b).

Table II. Morphological characteristics and mechanical properties of the MWNTs/Si₃N₄ composites as a function of the SPS parameters. (d = average Si₃N₄ grain size, AR = average Si₃N₄ aspect ratio, H = hardness, KIC = fracture toughness).

<table>
<thead>
<tr>
<th>Sample ID</th>
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<tr>
<td>α-phase (vol%)</td>
<td>80</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>D (nm)</td>
<td>190</td>
<td>230</td>
<td>290</td>
<td>240</td>
<td>250</td>
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<tr>
<td>AR</td>
<td>1.46</td>
<td>1.58</td>
<td>1.83</td>
<td>1.54</td>
<td>1.66</td>
</tr>
<tr>
<td>H (GPa)</td>
<td>18.3</td>
<td>16.7</td>
<td>16.5</td>
<td>16.6</td>
<td>17.1</td>
</tr>
<tr>
<td>KIC (MPa·m½)</td>
<td>4.4</td>
<td>5.1</td>
<td>5.3</td>
<td>4.7</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Apparent densities were measured by the Archimedes’ immersion method in water. The degree of $\alpha \rightarrow \beta$-Si₃N₄ transformation for each specimen was determined by X-ray diffraction (XRD) procedures. Microstructure was observed by scanning electron microscopy (SEM) over polished and etched specimens and on fracture surfaces. The average grain size and aspect ratio of the Si₃N₄ grains were estimated by image analysis methods on SEM micrographs, measuring at least 1000 features. Hardness (H) and fracture toughness (KIC) were assessed by Vickers indentation tests at 98 N and 196 N, respectively.

3. Results and discussion

Although fully dense (3.19 g·cm⁻³) composites were obtained for all the sintering conditions, the $\alpha \rightarrow \beta$-Si₃N₄ phase transformation degree depended on the sintering temperature (Table II). In this sense, for the specimen #1, sintered at the lowest temperature (1500 °C), most of the Si₃N₄ grains corresponded to $\alpha$-phase (80 vol%), while for the rest of specimens the percentage of $\alpha$-Si₃N₄ phase decreased down to 40 vol%. Conversely to Si₃N₄ materials sintered by other methods (pressureless sintering or hot-pressing), where densification and transformation occur simultaneously, in SPS-Si₃N₄ full sintering can take place without much $\alpha \rightarrow \beta$ transformation [5,7]. To get a complete transformation, temperature should be increased above 1550 °C. Nevertheless, changes in holding time, applied pressure or vacuum level did not affect to the phase transformation degree (Table II), supporting the fact that is a thermally activated transformation. For all SPS conditions no other crystalline phases were detected by XRD.
SEM observations evidenced that the microstructure of the specimens was mainly formed by Si$_3$N$_4$ grains of submicronic size surrounded by a glassy phase (Fig. 2).

The shape and size of Si$_3$N$_4$ grains depended on the SPS conditions. In this sense, specimen #1, sintered at 1500 ºC, presented equiaxial Si$_3$N$_4$ grains (Fig. 2a) with a very homogeneous grain size of 190 nm (Table II), similar to the original size of the powders (~ 200 nm [7]). However, the specimens sintered at 1550 ºC exhibited larger average grain size and aspect ratio (Table II and Fig. 2b and c). The increase in bimodality respect to the specimen #1 corresponded to a diminution on α:β phase ratio of the specimens. However, comparing only among the specimens sintered at 1550 ºC, the main SPS parameter promoting the grain growth and bimodality was the holding time, reaching maximum average grain size and aspect ratio values of 290 nm and 1.83, respectively for specimen #3 (Fig. 2c). Conversely, an increase in the applied pressure (specimen #4) or in the vacuum level (specimen #5) produced negligible microstructural differences.

The fracture surface of the specimens (Fig. 3) confirmed that MWNTs remained undamaged after the sintering processes and with a quite homogeneous dispersion into the Si$_3$N$_4$ matrix, although in some areas groups of individual nanotubes were also found.

The mechanical properties were mainly related to the α:β phase ratio and the matrix microstructural parameters. In this sense, the α-phase richest specimen (#1) presented the highest hardness value (18.3 GPa), which is in accordance with the typical hardness of α-Si$_3$N$_4$ materials [8]. The decrease on the α-phase content produced a reduction in hardness, showing comparable values for the rest of the specimens which were in the range 16.5 - 17.1 GPa. On the other hand, the increase on the Si$_3$N$_4$ grain size and, especially, in the aspect ratio led to higher fracture toughness values due to the development of the typical toughening mechanisms of this material, being the specimen #3, with the highest aspect ratio, the most crack growth resistant (5.3 MPa·m$^{1/2}$). It is important to point out that $K_{IC}$ values were quite above the data reported for Si$_3$N$_4$ materials having similar α:β phase ratio [9], which can be explained due to the reinforcement by the nanotubes.
Conclusions

$\text{Si}_3\text{N}_4$ composites containing 1 wt% of MWNTs were obtained by SPS with a quite homogeneous dispersion of the nanotubes into the matrix without signs of degradation. The lowest sintering temperature (1500 °C) was enough to promote full densification of a rich $\alpha$-$\text{Si}_3\text{N}_4$ phase specimen (80 vol%) with negligible grain growth. The increase on temperature allowed $\alpha \rightarrow \beta$-$\text{Si}_3\text{N}_4$ phase transformation up to 60 vol% of $\beta$-phase, accompanied by the matrix grain growth and the development of bimodality when the holding time was augmented. Changes in the applied pressure and the vacuum level did not produce significant modifications in the microstructures.

The richest $\alpha$-phase material presented the highest hardness and the lowest fracture toughness. Comparing pressureless sintering or hot-pressing specimens with similar $\alpha$/$\beta$ phase ratio, the increase in bimodality produced a higher fracture toughness value due to the occurrence of toughening mechanisms favoured by the presence of $\beta$-$\text{Si}_3\text{N}_4$ elongated grains and MWNTs into the material.

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References