Abstract

Titanium diboride (TiB₂) is a member of a specific group of materials known as ultra-high-temperature ceramics (UHTCs). UHTCs have a melting temperature greater than 3000°C and an ability to withstand in extreme environments at high temperatures. They have high hardness, high elastic modulus, high electrical and thermal conductivities, good thermal shock resistance and chemical inertness. The potential applications of UHTCs include atmospheric re-entry vehicles and hypersonic systems as nose caps and leading edges, high temperature resistant materials, corrosion resistant materials for furnaces, cathode materials for several metal processing, nozzle and armour materials and protective coating materials for hypersonic systems. In this study, graphene nanoplatelets (GNP) containing TiB₂ composites were prepared by spark plasma sintering (SPS) at 1700°C with a holding time of 5 min under 40 MPa. The effect of GNP addition on densification, microstructure, and mechanical properties of the composites were investigated. Oxidation behavior of the samples will also be evaluated.

1. Introduction

Ultra-high temperature ceramics (UHTCs) comprise materials which are binary compounds in which boron, nitrogen or carbon combine with one of transition metals (TMs) such as hafnium, titanium, zirconium, tantalum and niobium [1–3]. Also, UHTCs and their composites are member of the non-oxide, structural advance ceramics group [4]. They are characterized by good combination of high melting point (above 3000 °C), stiffness and hardness due to strong covalent bonding between TMs and boron, carbon or nitrogen. UHTCs also exhibit other important properties such as high refractoriness, high thermal and electrical conductivity, good thermal shock resistance, chemical inertness against molten metals or non-basic slags. The potential applications for UHTCs include use in corrosion resistance material for furnaces, high temperature-resistant materials, cathode for metal processing, atmospheric re-entry vehicles and hypersonic systems such as leading edges and nose caps [4,5]. Moreover, especially in aerospace applications, the development of ultra-high temperature composites with improved oxidation resistance and fracture toughness properties plays an important role.

Titanium diboride is a member of ultra-high temperature ceramics and displays key features of this group with its high melting point (3225 °C), low density (4.52 g/cm³), high hardness (25-35 GPa), high elastic modulus (>570 GPa), excellent thermal conductivity (60-120 W/m*K) and low electrical resistivity (10-30x10⁻⁶ Ω.cm). In spite of these eligible properties of this material, some limitations such as low fracture toughness, low oxidation resistance, poor flexural strength and low self-diffusion coefficient restrict their applications. Moreover its extremely high melting point and strong covalent bonding lead to high temperatures, so it is difficult to sinter by conventional sintering methods [5,6]. Several studies have been reported to improve fracture toughness, oxidation resistance and flexural strength of titanium diboride, by introducing second phase or appropriate sintering aids to TiB₂ matrix [6,7].

Graphene, which is incorporated many ceramic matrix composites, has sp² carbon atoms in a planar configuration and show distinguished characteristics such as remarkable mechanical strength, elasticity and unique thermal properties [5]. According to literature, ceramics can be converted to a tougher, stiffer, thermally conductive material by incorporated with graphene.

Spark plasma sintering (SPS) makes possible to densify ceramic based composites at a lower temperature and in a shorter time compared with conventional techniques. In the SPS technique, a pulsed direct current passes through graphite punch rods and dies simultaneously with a uniaxial pressure. The grain growth can be suppressed by rapid heating and the densification is accelerated at high temperature. Furthermore, the microstructure can be controlled by a fast heating rate and shorter processing times [6,7].
The objective of this study is to investigate the effect of graphene nanoplatelets addition on the microstructure and mechanical properties of spark plasma sintered TiB₂ ceramics. Properties of composites were examined systematically considering composition.

2. Experimental Procedure

The raw materials were commercially available titanium diboride (TiB₂, H.C. Starck, Grade D) with an average particle size 5.3 μm, and graphene nanoplatelets (GNP, Nanokomp, purity > 97, thickness: 5-8 nm, diameter: 5-10 mm). The raw materials were weighed correspond to the amount of 1, 5, and 10 vol% GNP. TiB₂ powder and GNPs were separately ball milled in ethanol for 24 h. Then, each powder was dispersed in ethanol by an ultrasonic homogenizer (Bandelin Sonopuls HD 2200, operating at 50% amplitude with on and off cycles) for 45 min. After dispersion of both TiB₂ powder and GNPs, powders were mixed together. Ultrasonic agitation (Hielscher UP400S, operating at 50% amplitude with on and off cycles) was used for 1 h to provide better dispersion behavior of powders before the ethanol evaporation. In drying oven, powder mixture was dried at 105 °C for 24 h. Pounding was applied in an agate mortar to get soft and unagglomerated powder mixture.

Starting powders were filled in a hollow cylinder graphite die (95 mm inner diameter, 50 mm thickness and a 50 mm height). For better conductivity, a graphite sheet was placed between the punches and the powder. The sintering was carried out using a spark plasma sintering (SPS) apparatus (7.40 MK-VII, SPS Syntex Inc.). The powder mixture with 0, 1, 5, and 10 vol% GNP contents were spark plasma sintered at 1700 °C for 5 min with a heating rate of 100 °C/min. A uniaxial pressure of 40 MPa and a pulsed direct current (12 ms/on, 2 ms/off) were applied during the entire SPS process under vacuum atmosphere. During cooling the uniaxial pressure was released. Current control mode was used in sintering of the specimens. For temperature control, an optical pyrometer (Chino, IR–AH) was used.

The bulk densities of the samples were measured by Archimedes principle and converted to relative densities using rule of mixtures. The crystalline phases were identified by X-ray diffractometry (XRD; MiniFlex, Rigaku Corp.) in the 2θ range of 10–80° at scanning rate of 2 °C/min. with CuKα radiation. Microstructure, morphology, oxidized and fracture surfaces of samples were examined using a scanning electron microscope (SEM; JEOL JSM 7000F) with an operating voltage of 5 kV. Sintered samples were polished before the SEM analysis.

The microhardness of the samples was measured using a microhardness tester (VHMOT, Leica Corp.) fitted with a Vickers indenter. Samples were grinded and polished before the measurements. Indentation was produced on the polished surfaces under a load of 9.8 N. The Vickers hardness of the samples were calculated. Indentation fracture toughness of the samples were calculated by Anstis equation from the half-length of crack formed around the indentations under load of 19.6 N.

The resistance to oxidation of monolithic sintered TiB₂, TiB₂-GNP composites was tested in stagnant air at temperatures of 1000-1400 °C for 90-360 min. A MoSi₂ resistance heated furnace (Nabertherm C42) was used to heat the samples. The samples were placed into the furnace at oxidation temperatures, and free cooling was applied.

3. Results and Discussion

The densification behavior of the specimens during SPS process was evaluated by displacement of punch rods displacement that occurs owing to shrinkage of the samples. These data were used to determine the starting and completion temperature of densification. The shrinkage of monolithic TiB₂ sample started at 1350 °C and stopped at 1665 °C.
~1470°C, and ~1450°C, respectively. The completion temperature for all composites is ~1700°C. When densification behaviors of composites were examined, it is clearly seen that shrinkage starting and completion times are related with amount of GNP and high volume content of GNP hinder the densification of TiB2-GNP composites. These results are compatible with literature [8].

The relative density values of TiB2-GNP composites were given in Table 1. According to data given in Table 1, increase in amount of GNP leads to increase relative density up to 98.6%. Monolithic sintered TiB2 has ~97% relative density, and 99T1G, 95T5G, 90T10G composites have relative density values 98%, 98.6% and 97.5 %, respectively. However, more than 5% vol. GNP addition caused to decrease in relative density from ~98.6 to ~97.5%. Relative density values are compatible with densification behavior of powders during sintering process.

<table>
<thead>
<tr>
<th>TiB2 (vol.%)</th>
<th>GNP (vol.%)</th>
<th>Relative Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-</td>
<td>97.0</td>
</tr>
<tr>
<td>99</td>
<td>1</td>
<td>97.6</td>
</tr>
<tr>
<td>95</td>
<td>5</td>
<td>98.0</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>97.5</td>
</tr>
</tbody>
</table>

Table 2 demonstrates the effect of GNP content on the Vickers hardness of TiB2 composites at loads of 9.8 N. According to calculated hardness results, TiB2 samples which were sintered at 1700°C with a relative density of ~97% had a hardness of ~24 GPa. Moreover, hardness results were in the range of ~17-20 GPa for TiB2-GNP binary composites. Increase amount of GNP caused to decrease in hardness results. This could be explained by differences of theoretical hardness value of TiB2 and GNP. The effect of GNP content on the fracture toughness values of TiB2-GNP composites were calculated by Anstis equation and shown also in Table 2. Fracture toughness result was calculated as ~3.9 MPa·m^{1/2} for monolithic sintered TiB2. A gradual increase in the fracture toughness values was observed for the sample with 10 vol.% GNP addition whereas other additions do not show a significant change in fracture toughness values, as shown in Table 2. In order to determine the toughening mechanisms, interaction between crack propagating and microstructure was analyzed. GNP inhibits the crack propagation and led the crack deflection. Moreover, this phenomenon provides the reduction in the energy of crack as an energy dissipating mechanism. The intrinsic GNP energy dissipating mechanisms can thus be translated into toughening mechanism.

<table>
<thead>
<tr>
<th>Code</th>
<th>Hardness (GPa)</th>
<th>Fracture Toughness (MPa·m^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>100T</td>
<td>24.2 ± 0.7</td>
<td>3.9 ± 0.4</td>
</tr>
<tr>
<td>99T1G</td>
<td>20.6 ± 0.6</td>
<td>3.6 ± 0.6</td>
</tr>
<tr>
<td>95T5G</td>
<td>18.2 ± 0.3</td>
<td>3.7 ± 0.6</td>
</tr>
<tr>
<td>90T10G</td>
<td>17.2 ± 0.6</td>
<td>4.1 ± 0.6</td>
</tr>
</tbody>
</table>

Fig. 3 shows the fracture surface microstructures of TiB2-GNP composites with 1 and 10 vol.% GNP. Dense and mostly uniform microstructures were observed. The GNP wrapped around the matrix grains and conformed to the shapes of TiB2 grain boundaries. Overlapping and agglomerated GNP and the separation of matrix grains were also seen.
Fig. 3. SEM images of the fracture surfaces of the TiB$_2$-GNP composites with (a) 1 vol.%, and (b) 10 vol.% GNPs.

4. Conclusion

TiB$_2$-GNP composites were produced by SPS at 1700°C, under 40 MPa with 300 holding time. The addition of GNP does not significantly change the relative densities. The TiB$_2$-GNP composites with 5 and 10 vol.% GNP reached maximum relative density and fracture toughness results as ~98% and ~4.1, respectively. Vickers hardness of TiB$_2$-GNP composites decreased with increasing GNP content from ~24 to ~17 GPa and highest hardness was achieved with the addition of 1 vol.% GNP.

Acknowledgements

The financial support for this research by the Scientific and Technological Research Council of Turkey (TUBITAK) with a project number of 215M617 is gratefully acknowledged. Authors thank to H.H. Sezer and B. Yavas for microstructural investigations and SPS experiments, respectively.

References


