Spark Plasma Sintering Techniques Improve the Properties of AlN-TiB$_2$ Ceramics with Nb$_2$O$_5$, Y$_2$O$_3$ and ZrO$_2$ as a Sintering Precursors

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Abstract  
AlN-TiB$_2$ composites ceramics were prepared by Spark Plasma Sintering (SPS). The effects of Nb$_2$O$_5$, Y$_2$O$_3$, and ZrO$_2$ additives on mechanical properties and densification were investigated. X-ray diffraction was used to identify the phases in the resulting composites. Good densification results were obtained using the different sintering additives. The mechanical properties such as hardness and fracture toughness were obtained using a Vickers indentation, the maximum values of hardness and fracture toughness were 13.9 ± 0.4 GPa for A4TN (90.48% AlN-4.76% TiB$_2$-4.76% Nb$_2$O$_5$, wt% of composite ceramic) and 5.8 ± 0.9 MPa.m$^{-1/2}$ for A23TZ (71.43% AlN-23.81% TiB$_2$-4.76% ZrO$_2$, wt% of composite ceramic).

Keywords: Sintering; Densification; Grain growth; Microstructure-property relationship; Spark plasma sintering technique

Introduction

Researchers specializing is materials science continue developing improved and more versatile ceramics for advanced technological applications. The high thermal conductivity and corrosion resistance of aluminum nitride (AlN) in combination with the high hardness and electrical conductivity of titanium diboride (TiB$_2$) allows us to consider the composite AlN-TiB$_2$ as a promising wear and corrosion resistant ceramics, besides they can be used as the thermocouple protection tube [1,2].

Aluminium Nitride (AlN) ceramics have attracted interest due to their high thermal conductivity and good electrical properties. Their thermal conductivity varies between 80 and 260 Wm$^{-1}$K$^{-1}$. They exhibit good electrical insulation and have a low dielectric constant (9 at 1 MHz), high thermal conductivity and low thermal expansion coefficient (4.4 x 10$^{-6}$ K$^{-1}$) [3]. AlN-based materials have a wide field of applications in structural and refractory areas [4].

Titanium diboride (TiB$_2$) is a material of growing interest among various ultra-high temperature ceramics (UHTC) due to its characteristic high melting point (~3225°C), low density (4.5 g/cm$^3$), high hardness (25 GPa), high thermal conductivity (96 W/mK), and electrical conductivity (22 x 10$^6$ Ω$^{-1}$cm$^{-1}$). Low thermal expansion coefficient (7.4 x 10$^{-6}$ K$^{-1}$) and high wear resistance [5]. These excellent properties makes it attractive for many high-temperature structural applications [6]. The densification of monolithic TiB$_2$ requires extremely high sintering temperatures of up to ~2100°C and long holding times due to the predominance of covalent bonding and the low self-diffusion coefficient. Such extreme processing conditions result in exaggerated grain growth of the as-sintered materials, leading to degradation of mechanical properties [7,8].

One way to sinter these materials is through an advanced sintering method such as Spark Plasma Sintering (SPS). During the SPS process, by virtue of special heat effects such as joule heat, electromagnetic field and electrical discharge, highly densified ceramics are obtained at relatively low temperature, in a very short sintering time and with uniform heating for sintered bodies. Functional materials, ceramics, cermets, intermetallic compounds, and so on [9] have been processed by this method.

In this study, for the first time, composites of AlN-TiB$_2$ were sintered by SPS to evaluate the applicability of SPS techniques in sintering the AlN-TiB$_2$ composites. The effect of the Nb$_2$O$_5$, Y$_2$O$_3$, and ZrO$_2$ content, used as sintering additives, on mechanical properties and densification of composites were also studied in detail.

Materials and Methods

Raw materials

Commercially available AlN powder (grade A100 WR, available from Advanced Refractory Technologies, Buffalo, N. Y., USA), TiB$_2$ powder (98.64 wt%, Storchem, Inc., Burlington, ON, Canada), were used as raw materials. Nb$_2$O$_5$, Y$_2$O$_3$ powder (99.5 wt%, Strem Chemicals, Newburyport, MA, USA), ZrO$_2$ powder (99 wt%, Strem Chemicals, USA) and Y$_2$O$_3$ powder (99.99 wt%, Strem Chemicals, USA) were used as sintering additives. The sample compositions studied in this work are shown in Table 1.

Experimental procedure

Powders were homogenized by stirring in a plastic bottle for 4 hours with acetone as dispersant and then were ball milled in a plastic bottle for 25 min with absolute isopropanol as dispersant. After mixing and drying, each of the resulted powders was put into a graphite die of 20 mm in diameter and then sintered in a SPS equipment (Dr. SINTER SPS-1050-CE). During SPS process, both heating and cooling rate were controlled at 150°C/min for all samples. A pressure of 60 MPa from the beginning to the end of the sintering cycle was applied. After 10 min of holding time, samples of 20 mm in diameter and thickness in the 6.9-
forms rutile (TiO$_2$) and boron oxide (B$_2$O$_3$), according to the following reaction [11]:

$$2\text{TiB}_2(s) + 5\text{O}_2(g) \rightarrow 2\text{TiO}_2(s) + 2\text{B}_2\text{O}_3(s) \quad (1)$$

While the surface of AlN is oxidized, alumina (Al$_2$O$_3$) and nitrogen (N$_2$) are formed, according to the following reaction (2):

$$4\text{AlN}(s) + 3\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s) + 2\text{N}_2(g) \quad (2)$$

Table 2 and Figure 1 show the relative density of the obtained composites. It can be observed that as the amount of TiB$_2$ increases, the relative density decreases, these results confirm again the difficulty to sinter TiB$_2$. For the samples with NbO$_2$, the densities obtained were 97% for the sample A4TN, 94% for A14TN and 95% for A23TN. The samples with Y$_2$O$_3$ were sintered at 1850°C, obtaining densities of 96% for A4TY, 97% for A14TY and 92% for A23TY by the formation of a liquid phase. ZrO$_2$ was found to be the best sintering additive for the AlN-TiB$_2$ obtaining densities of 100% for A4TZ, 99% for A14TZ and 94% for A23TZ.

As shown in Figure 1, the best densification results were obtained with a small amount of TiB$_2$ as the content of TiB$_2$ increased the percentage of densification decreased drastically.

**Crystalline Phases**

Figure 2 shows the XRD pattern for samples A23TN, A14TN and A4TN sintered by spark plasma sintering at 1950°C for 10 min at an applied pressure of 60 MPa in argon atmosphere. The XRD analysis shows that AlN and TiB$_2$ are the main phases of all composites. Niobium diboride (NbB$_2$), niobium nitride (NbN, only in A4TN), alumina (Al$_2$O$_3$), hexagonal boron nitride (hBN), aluminum diboride (AlB$_2$) and titanium nitride (TiN) were identified. The possible reactions for the production of NbB$_2$, NbN, Al$_2$O$_3$ and TiN in the system could be represented as follows:

$$\text{NbO}_2(s) + 1.2\text{AlN}(s) \rightarrow 1.6\text{NbB}_2(s) + 0.6\text{Al}_2\text{O}_3(s) + 0.4\text{NbN}(s) + 0.4\text{N}_2(g) \quad (3)$$

$$\text{NbB}_2(s) + \text{TiB}_2(s) \rightarrow \text{NbB}_2(\ell) + \text{TiO}_2(\ell) \quad (4)$$

$$3\text{TiO}_2(s) + 4\text{AlN}(s) \rightarrow 3\text{TiN}(s) + 2\text{Al}_2\text{O}_3(\ell) + \frac{7}{2}\text{N}_2(g) \quad (5)$$

Sairam, et al. [12], obtained NbB$_2$ by spark plasma sintering at

**Table 1: Materials compositions and sintering parameters.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Starting powders (wt. %)</th>
<th>Preparation Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AlN</td>
<td>TiB$_2$</td>
</tr>
<tr>
<td>A4TN</td>
<td>90.48</td>
<td>4.76</td>
</tr>
<tr>
<td>A14TN</td>
<td>80.95</td>
<td>14.29</td>
</tr>
<tr>
<td>A23TN</td>
<td>71.43</td>
<td>23.81</td>
</tr>
<tr>
<td>A4TY</td>
<td>90.48</td>
<td>4.76</td>
</tr>
<tr>
<td>A14TY</td>
<td>80.95</td>
<td>14.29</td>
</tr>
<tr>
<td>A23TY</td>
<td>71.43</td>
<td>23.81</td>
</tr>
</tbody>
</table>

**Table 2: Densities values of the produced composites.**

<table>
<thead>
<tr>
<th>Composites</th>
<th>Theoretical density (g/cm$^3$)</th>
<th>Measured density (g/cm$^3$)</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90.48% AlN – 4.76% TiB$_2$ – 4.76% NbO$_2$ (A4TN)</td>
<td>3.45</td>
<td>3.35</td>
<td>97</td>
</tr>
<tr>
<td>80.95% AlN – 14.29% TiB$_2$ – 4.76% NbO$_2$ (A14TN)</td>
<td>3.59</td>
<td>3.38</td>
<td>94</td>
</tr>
<tr>
<td>71.43% AlN – 23.81% TiB$_2$ – 4.76% NbO$_2$ (A23TN)</td>
<td>3.50</td>
<td>3.32</td>
<td>95</td>
</tr>
<tr>
<td>90.48% AlN – 4.76% TiB$_2$ – 4.76% Y$_2$O$_3$ (A4TY)</td>
<td>3.50</td>
<td>3.36</td>
<td>96</td>
</tr>
<tr>
<td>80.95% AlN – 14.29% TiB$_2$ – 4.76% Y$_2$O$_3$ (A14TY)</td>
<td>3.43</td>
<td>3.32</td>
<td>97</td>
</tr>
<tr>
<td>71.43% AlN – 23.81% TiB$_2$ – 4.76% Y$_2$O$_3$ (A23TY)</td>
<td>3.62</td>
<td>3.32</td>
<td>92</td>
</tr>
<tr>
<td>90.48% AlN – 4.76% TiB$_2$ – 4.76% ZrO$_2$ (A4TZ)</td>
<td>3.39</td>
<td>3.38</td>
<td>100</td>
</tr>
<tr>
<td>80.95% AlN – 14.29% TiB$_2$ – 4.76% ZrO$_2$ (A14TZ)</td>
<td>3.41</td>
<td>3.38</td>
<td>99</td>
</tr>
<tr>
<td>71.43% AlN – 23.81% TiB$_2$ – 4.76% ZrO$_2$ (A23TZ)</td>
<td>3.58</td>
<td>3.37</td>
<td>94</td>
</tr>
</tbody>
</table>
The presence of hBN and TiN, attributed to the reaction of N2 (reactions 3 and 5) with TiB2:

\[ \text{TiB}_2(g) + \frac{1}{2} \text{N}_2 \rightarrow \text{TiN}(s) + 2 \text{BN}(s) \]  

(6)

The presence of AlN and TiN, attributed to the following reaction:

\[ \text{TiB}_2(s) + \text{AlN}(s) \rightarrow \text{AlB}_2(s) + \text{TiN}(s) \]  

(7)

In reaction (7) the aluminum diboride was assigned the formula "AlB2", it was found that the density of such phase was 2.955 g/cm³, which corresponds to Al0.9B2, not to AlB2, which has a theoretical density of 3.17 g/cm³ [13].

Figure 3 shows the XRD pattern for samples A23TY, A14TY and A4TY sintered by spark plasma sintering at 1850°C for 10 min at an applied pressure of 60 Mpa in an argon atmosphere. The XRD analysis showed that AlN and TiB2 are the main phases. However, Al0.9B2 was identified as a secondary phase in all samples, i.e. YAlO3 (YAG) in A4TY and A14TY, AI2O3 (YAP) in A14TY and A23TY. In addition, TiN and BN were found in samples A14TY and A23TY. No peaks of TiN and BN were found in samples A4TY.

The existence of TiN and BN in the samples A14TY and A23TY can be related to the presence of TiO2 in the surface layer of the TiB2 particles, which reacted with the AlN in the sintering process according to the reaction (5), the N2 from nitride reacted with TiB2 according to reaction (6). Only a limited amount of TiN and BN was formed in the sintering process under argon, since only a limited amount of TiO2 was available [14].

Figure 4 shows the XRD pattern for samples A23TZ, A14TZ and A4TZ sintered by spark plasma sintering at 1950°C for 10 min at an applied pressure of 60 Mpa under an argon atmosphere. The XRD analysis showed that AlN and TiB2 were the main phases for all composites. As secondary phases, zirconium nitride (ZrN), alumina (Al2O3), boron nitride (BN) and titanium nitride (TiN) were identified. Aluminum diboride (Al0.9B2) was identified in samples A23TY and A14TY.

The real process to explain the presence of ZrN is complex but it should be modeled with the following reactions [15]:

\[ 4\text{AlN}(s) + 3\text{ZrO}_2(g) \rightarrow 3\text{ZrN}(s) + 2\text{Al}_2\text{O}_3(s) + \frac{1}{2}\text{N}_2(g) \]  

(8)

\[ 2\text{AlN}(s) + 2\text{ZrO}_2(g) \rightarrow 2\text{ZrN}(s) + 2\text{Al}_2\text{O}_3(s) + \frac{1}{2}\text{O}_2(g) \]  

(9)

### Microstructural Analysis

Figure 5a-5c shows SEM micrographs of polished surfaces of the A4TN, A14TN and A23TN composites, respectively. It was observed in Figure 5 that AlN-TiB2-Nb2O5 ceramics were mainly composed of three dark, gray and white phases. The elemental composition was obtained through EDS analysis at point A and point B in Figure 5a, as shown in Figure 6. The EDS of Figure 6a and 6b revealed that the dark phase content of the composite ceramics.
phase, point A in Figure 5a, consisted mostly of Al and N elements and the gray phase, point B in Figure 5a, predominantly contained Ti and B elements, indicating that the dark phase was AlN and the gray phase TiB$_2$.

Some white phases were also observed among the AlN grains and TiB$_2$ grains in the composites A4TN, A14TN and A23TN (marked with arrows in Figure 5). In order to deeply clarify the phases, EDS analyses were employed (Figure 7). It was concluded with the support of XRD patterns, SEM-EDS that AlN, TiB$_2$, NbB$_2$, NbN, were found in A4TN. Al$_2$O$_3$, hBN, Al$_{0.9}$B$_2$ and TiN phases were observed in A4TN, A14TN and A23TN composites.

Figure 8a-8c shows SEM micrographs of polished surfaces of the AlN-TiB$_2$-Y$_2$O$_3$ composites with different amounts of TiB$_2$, A4TY, A14TY and A23TY. The AlN grains were composed of a yttria-based secondary phase. TiB$_2$ grains were randomly dispersed in the AlN matrix. EDS analyses showed that dispersed gray particles are TiB$_2$. 

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The grain pattern was observed on polished surfaces of composite ceramics.

According to the EDS analyses (Figure 9) the white particles, were attributed to yttria-based secondary phase (marked with arrows in Figure 8a-8c). As shown in Figure 8, the presence of Y2O3 as a sintering additive forms with Al2O3, from the Surface of AlN, an eutectic composition that helps sintering and normally precipitates as YAG, diffuses between the particles, which helps to achieve highly dense materials. The interesting point is to observe that the results of the densification are not very high in comparison with other oxides used as additives, this may be due to the fact that grain growth is controlled by diffusion at the grain edge.

Figure 10a-10d displays the SEM micrographs of polished surfaces of the composites A4TZ, A14TZ and A23TZ, respectively. From this figure, it is observed that AlN-TiB2 composite was mainly composed of three phases. The chemical composition of the gray and dark zones were identified by EDS. Several white phases were observed among AlN and TiB2 grains (see arrows in Figure 10a-10c), these analyzed by EDS (Figure 11). The results revealed that the microstructure consists predominantly of zirconium. Therefore it was concluded with supports
of XRD patterns, and SEM-EDS that AlN, TiB₂, ZrN, Al₂O₃, BN and TiN phases are the main contributors of the three composites, besides the phase Al₀.₉B₂ was found only in the A14TZ and A23TZ composites.

Mechanical Properties

Table 3 shows the mechanical properties of the sintered composites. The hardness results for all composites were found to be above to that of the monolithic AlN, but well below to the magnitude of the TiB₂ value. The fracture toughness of the composites was improved when compared to the value of the monolithic AlN. The composites A23TN, A14TZ and A23TZ showed higher fracture toughness, surpassing the fracture toughness value of the monolithic TiB₂. The fracture toughness of the composites, exceeded the values reported in our previous paper, using the same amount of Nb₂O₅, Y₂O₃ and ZrO₂ [16,17].

Figure 12 shows the hardness and fracture toughness measurements for the sintered samples. It is noteworthy that all the samples have a higher hardness that of the monolithic AlN due to the contribution of TiB₂ phase. A significant increase of the hardness was observed in the samples that contain Nb₂O₅ (A4TN, A14TN and A23TN), this could be a consequence of a remarkable presence of nitrides, identified by the XRD spectrum. The presence of a mixture of NbB₂ [10] and NbN phases [18] increased the hardness. It can also be observed that as the amount of TiB₂ increased to 14.29 wt.%, the hardness in the samples sintered with Nb₂O₅ and ZrO₂ decreased, being attributed to the high covalent character of TiB₂ and its difficulty to be sintered properly, increasing the porosity and the grains growth, reducing the density and hardness. In the sample sintered with Y₂O₃, it was observed that as the amount of TiB₂ increased, the hardness also increased. This result was associated to the formation of a secondary liquid phase (YAG and YAP), which diffuses between the grains of AlN and TiB₂, acting as an elastic interface.

Table 3: Results of the mechanical properties for the composites.

<table>
<thead>
<tr>
<th>Composites</th>
<th>Hv (GPa)</th>
<th>KIC (MPa.m½)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>10.6 a</td>
<td>3.2 a</td>
</tr>
<tr>
<td>TiB₂</td>
<td>25 a</td>
<td>5.2 a</td>
</tr>
<tr>
<td>A4TN</td>
<td>13.9 ± 0.4</td>
<td>4.3 ± 0.4</td>
</tr>
<tr>
<td>A14TN</td>
<td>12.8 ± 0.5</td>
<td>4.4 ± 0.6</td>
</tr>
<tr>
<td>A23TN</td>
<td>13.1 ± 0.4</td>
<td>5.4 ± 0.9</td>
</tr>
<tr>
<td>A4TY</td>
<td>10.7 ± 0.2</td>
<td>4.5 ± 0.6</td>
</tr>
<tr>
<td>A14TY</td>
<td>11.5 ± 0.4</td>
<td>4.7 ± 0.6</td>
</tr>
<tr>
<td>A23TY</td>
<td>11.9 ± 0.4</td>
<td>4.8 ± 0.9</td>
</tr>
<tr>
<td>A4TZ</td>
<td>12.7 ± 0.3</td>
<td>3.8 ± 0.4</td>
</tr>
<tr>
<td>A14TZ</td>
<td>12.4 ± 0.3</td>
<td>5.5 ± 0.8</td>
</tr>
<tr>
<td>A23TZ</td>
<td>12.9 ± 0.3</td>
<td>5.8 ± 0.9</td>
</tr>
</tbody>
</table>

a,b Values taken from the reference [3,17], respectively.
Conclusions

The sintering of AlN-TiB2 with Nb2O5, Y2O3 and ZrO2 as sintering additives, was achieved by SPS, obtaining excellent densification results, increasing the values of hardness and fracture toughness with respect to the monolithic AlN. The ceramic composites that showed the best densification results were A4TZ and A14TZ, with values up to 100% of theoretical density.

With respect to mechanical properties, higher values of hardness and fracture toughness were obtained when compared to those of the monolithic AlN. The composites that showed the highest hardness were A4TN and A23TN, with values of 13.9 ± 0.4 GPa and 13.1 ± 0.4 GPa, respectively. Regarding fracture toughness, it was observed that it increased when the amount of TiB2 increased. Therefore, the composites with a content of 23.81% of TiB2 showed the best results.

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