Effect of tungsten disilicide addition on tungsten boride based composites produced by milling-assisted pressureless sintering

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ABSTRACT
In this study, tungsten boride (WB and W5B) based composites with various amounts of tungsten disilicide (WSi2) addition were fabricated by using a combined method of mechanical milling (MM), cold isostatic pressing (CIP) and pressureless sintering (PS). MM was conducted for 4 h in ethanol (wet milling) and Argon atmosphere (dry milling) using a high-energy ball mill. WSi2 was used with different amounts (0, 5, 10 and 20 wt.%) in order to investigate its effect on the resultant products. MM’d powders were compacted using CIP under a pressure of 450 MPa, and were consecutively sintered at 1600 °C for 2 h and 1770 °C for 2 h under Ar atmosphere. Compositional, physical and microstructural characterizations of the samples were performed using stereo and optical microscopes, X-ray diffractometer, TOPAS software, scanning electron microscope coupled with an energy-dispersive spectrometer, particle size analyzer and gas pycnometer. Sintered products were also characterized in terms of Archimedes density and Vickers microhardness. Moreover, the oxidation studies of the samples were performed at 500 and 1000 °C via thermogravimetric analyzer. The results showed that the highest density, microhardness and oxidation stability values amongst the fabricated composites were obtained for the dry milled and sintered WB-20 wt.% WSi2 sample.

1. Introduction
High temperature structural ceramics such as borides, carbides, nitrides and silicides are good candidates for advanced applications thanks to their exceptional properties like high melting temperature, high hardness, high thermal conductivity and good corrosion resistance [1-3]. There are ample literature reported on the improvement of these ceramics in terms of densification, mechanical and physical properties, oxidation resistance and ablation resistance, by applying composite approaches [1,4-6] ZrB2 and HfB2 can be shown as examples of the most studied ceramic composites [4,5,7]. However, other borides can also be promising ceramics and worth investigating. Among transition metal borides, tungsten borides have potential usage for industrial applications at extreme environmental conditions. WB (2665 °C) and W5B (2670 °C) are the most stable tungsten boride phases in the W-B binary phase diagram (containing WB, W5B, W10B5, W5B5 and WB6 phases) [8-10]. They exhibit interesting properties such as high melting points, high hardness values, high abrasion resistances, chemical inertness, magnetic and electrical properties and thermal shock resistances [10-13]. Furthermore, transition metal silicides are important materials due to their high temperature oxidation resistance and mechanical properties. Amongst them, tungsten disilicide (WSi2) can be a good candidate as a reinforcement material thanks to its abrasive, adhesive wear and oxidation resistances [14,15]. In this manner, composites including boride and silicide phases may offer improved mechanical properties, oxidation and corrosion resistance, particularly at high temperatures [16-18]. As one kind of boride and silicide composite, WB-WSi2 composites are promising as advanced structural materials. There are only few attempts for sintering of tungsten boride in the literature [19-22]. Grabis et al. fabricated WB and B5C composites by spark plasma synthesis from W, C and amorphous B blends [20]. Kuzenkova et al. studied pressureless sintering of WB5 at 1700 °C and indicated that WB5 phases decomposed into WB and B (which was further oxidized) phases [21]. In the study of Hamamoto et al., WB and W5B5 powders

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which contained amorphous B and different amounts of W powders were sintered by hot-pressing method [23]. In another study, ultrapure WB powders were hot-pressed at different pressure (1-3 GPa) and temperature (700-1000 °C) values for 60 min, and high dense WB samples were produced [22]. Recently, Fan et al. reported a study on the theoretical assessments of WB phase and also some investigations on its physical and mechanical properties [24]. As a result of this study, they proposed the WB as a promising material for industrial applications as coatings, hard alloy tools and ceramics. However, there are no studies published about sintering of WB or WB based composites.

In the present study, the effect of WSi₂ addition (0, 5, 10 and 20 wt.%) was investigated on tungsten boride matrix for the first time, using mechanical milling, cold isostatic pressing and pressureless sintering methods. Sintered samples were characterized in regard of microstructure, density, microhardness and oxidation stability. This study will contribute to the archival literature and further investigations about tungsten boride based composites.

2. Materials and methods

2.1. Raw materials and powder preparation

In the experimental studies, commercial WB (Alfa Aesar, -325 mesh, 99 % purity) and WSi₂ (Alfa Aesar, -325 mesh, 99.5 % purity) powders were used. WSi₂ powders were added into the WB matrix with the amounts of 0, 5, 10 and 20 wt.%. Milling experiments were conducted in a Fritsch Pulverisette 5 planetary ball mill, and milling parameters were presented in Table 1. Milling performed in absolute ethanol (Merck) was referred as wet milling whereas milling carried out under Ar (Linde) atmosphere was referred as dry milling. After wet milling, powders were dried at 100 °C for 12 h. Powders for dry milling experiments was handled in a Plaslabs glove box.

<table>
<thead>
<tr>
<th>Type of parameter</th>
<th>Value/Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed</td>
<td>400 rpm</td>
</tr>
<tr>
<td>Capacity of vial</td>
<td>500 ml</td>
</tr>
<tr>
<td>Diameter of ball</td>
<td>10 mm</td>
</tr>
<tr>
<td>Vial and ball material</td>
<td>Yttria stabilized zirconia</td>
</tr>
<tr>
<td>Ball-to-powder weight ratio</td>
<td>20:1</td>
</tr>
<tr>
<td>Milling time</td>
<td>4 h</td>
</tr>
<tr>
<td>Milling atmosphere</td>
<td>Ar or absolute ethanol</td>
</tr>
</tbody>
</table>

2.2. Consolidation and sintering

Wet and dry milled powders were placed in silicon cylindrical molds having 6 mm diameter and height. Cold isostatic pressing (CIP) was applied to the molds under 450 MPa pressure. Compacted powders were sintered under Ar atmosphere in a Linn HT-1800 high-temperature controlled-atmosphere furnace according to the sintering regime given in Figure 1(a). For thermogravimetric analyses (TGA), powders were consolidated into cylindrical preforms with a diameter of 4 mm using a MSE cold press (CP) under a uniaxial pressure of 450 MPa. Specimens consolidated by CIP and CP were presented in Figure 1(b) and (c), respectively.

2.3. Characterization

Phase characterizations of the milled powders and sintered samples were performed using a Bruker D8 Advanced Series X-ray diffractometer (XRD) with CuKα (1.54060 Å) radiation with 2θ value of 20-90° and step size of 2°/min. Bruker® Diffracplus EVA software was utilized to identify crystalline phases in the XRD patterns using the International Centre for Diffraction Database (ICDD) PDF-2 2016. Average crystallite sizes and lattice strains of the milled powders were calculated using TOPAS 4.2 (Bruker AXS) software [25]. Average particle sizes of the milled powders were

Figure 1. (a) Sintering regime, and SM images of the samples sintered by, (b) CIP, and (c) CP.
determined using a Microtrac Nano-flex particle size analyzer (PSA) equipped with a Bandelin Sonopuls ultrasonic homogenizer. Pycnometer densities of the milled powders were measured by a Micromeritics AccuPyc II 1340 gas pycnometer at room temperature using He gas (Linde) as the displacement medium.

General low-magnification images of the consolidated samples were taken using a Zeiss Discovery V12 stereomicroscope (SM) coupled with a Zeiss Axiocam ERC5s high resolution digital camera. Microstructural characterizations of the sintered samples were carried out using a Nikon Eclipse optical microscope (OM) and a Jeol-JCM-6000 benchtop (SEM) coupled with an energy-dispersive spectrometer (EDS). Densities of the sintered samples were determined using the Archimedes method. Microhardness values of the sintered samples were obtained under the load of 200 g for 10 sec, and each sample included the mean value of 20 measurements and standard deviation. Moreover, the oxidation studies of the cold pressed and sintered samples were carried out at 500 and 1000 °C by TGA with heating rate of 10 °C/min and airflow of 200 ml/min.

3. Results and discussion

3.1. Characterization of the milled powders

Figure 2(a) and (b) show the XRD patterns of the 4 h of dry milled and wet milled WB-x wt.% WSi₂ (x=0, 5, 10 and 20) powders. There are only WB (ICDD card no: 73-1769, Bravais lattice: body-centered tetragonal, a=3.11 nm and c=16.93 nm) and WSi₂ (ICDD card no: 81-2168, Bravais lattice: body-centered tetragonal, a=3.21 nm and c=7.84 nm) phases. As expected, XRD intensity of the WSi₂ phase increased with its increasing amount. Comparing the XRD patterns of the dry and wet milled powders for the fixed WSi₂ amount, it can be clearly seen that the lack of ethanol in milling environment resulted in broader WB and WSi₂ peaks. Besides, the XRD intensities of the phases, especially WSi₂, are higher for the wet milled samples. This indicated higher amount of decrease in grain sizes at dry milling conditions in which high impact energy created by the effect of continuous collisions between balls, vial and particles. On the other hand, the presence of ethanol can limit the transfer of the impact energy to the powder particles. Furthermore, any formation of secondary phases and any contamination were not observed after dry and wet milling within the detection limit of the used diffractometer (> 2 wt.%).

Based on the XRD patterns in Figure 2(a) and (b), average crystallite sizes and lattice strains of the powders were determined taking into account the highest three peaks of the WB phase (reflections from (103), (105) and (112) planes at the 2θ values of 32.8, 39.3 and 42.48°). The average crystallite sizes and lattice strains of the WB phase in the milled powders are given in the Table 2. According to these results, the milling environments affected the crystallite size and strain values of the powders. Dry milled samples had smaller average crystallite size and higher lattice strain than those of wet milled ones. However, any significant difference was not observed in these values for both milling conditions as WSi₂ amount increased up to 20 wt.%. These findings are compatible with their XRD patterns. Moreover, average particle sizes of the dry milled powders were found around 350 nm whereas those of wet milled ones were around 500 nm (Table 2). These results showed that particle size was more effectively reduced in dry milling condition than that of wet milling for the studied ceramic system. A similar tendency was reported by Jung et al. for boron particles [26]. According to Table 2, pycnometer densities of the milled powders were about 10-20% lower than their theoretical densities. The refinement of the particle sizes created vacancies and dislocations in the crystallite boundaries or subgrain boundaries [27]. This can be shown as the probable reason of the dif-
The difference between theoretical and pycnometer densities of the milled powders.

3.2. Characterization of the sintered products

Figure 3(a) and (b) illustrate the XRD patterns of the dry and wet milled, and sintered WB-x wt.% WSi₂ (x=0, 5, 10 and 20) samples. In these patterns, WB (ICDD card no: 73-1769, Bravais lattice: body-centered tetragonal, a=3.11 nm and c=16.93 nm), W₂B (ICDD card no: 025-0990, Bravais lattice: body-centered tetragonal, a=5.57 nm and c=4.74 nm) and WSi₂ (ICDD card no: 081-2168, Bravais lattice: body-centered tetragonal, a=3.21 nm and c=7.84 nm) were detected. Besides, the XRD patterns of the wet milled and sintered products (Figure 3(b)) revealed a very small amount of ZrO₂ phase (ICDD card no: 65-1024, Bravais lattice: primitive monoclinic, a=5.14 nm, b=5.21 nm and c=5.31 nm) arose from the wear of milling media. Similarly, there were some studies showing that wet milling caused more contamination than dry milling [26,28]. On the other hand, in another study about the milling media contamination, it was reported that yttria stabilized zirconia milling media provided the lowest contamination amongst hardened steel, tungsten carbide, partially stabilized zirconia, yttria stabilized zirconia and alumina vial and balls [29]. The W₂B phase was found as a dominant phase both in the XRD patterns of the wet and dry milled and sintered WB samples without WSi₂ addition. This means that some amount of WB has high affinity for transformation into the W₂B phase (lowest boride in the binary phase diagram) by the effect of sintering temperature. It was already reported that W₂B phase initiated at 1000 °C and its amount increased up to 1500 °C without any formation of other W borides [8,9]. Also, the formation of higher tungsten borides (WB, W₄B and W₅B) were found favorable at temperatures below 1000 °C [9]. There should be some amount of B phase revealed during the formation of W₂B phase. However, any free B was not detected in the XRD patterns probably due to its non-crystalline structure or very small amount. The negative effect of amorphous B on the sintering of tungsten boride powders was previously reported [21]. Also, it can be said that wet milling promoted the formation of W₂B phase more than dry milling, based on the comparison of their peak intensities. According to Figure 3(a) and (b), it can comprehended that WSi₂ addition has a positive effect on the stability of WB phase. As the amount of WSi₂ increased from 0 to 20 wt.%, the peak intensities of W₂B phase decreased and those of WB phase increased. The dominant phase was WB for 20 wt.% WSi₂ added samples sintered from both dry and wet milled powders.

Table 2. Average crystallite sizes, lattice strains, particle sizes, theoretical and pycnometer densities of the dry and wet milled powders.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Dry Milling</th>
<th>Addition of WSi₂ (wt.%)</th>
<th>Wet Milling</th>
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<tbody>
<tr>
<td>Crystallite Size (nm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>10.2</td>
<td>15.8</td>
<td>19.5</td>
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<tr>
<td>5</td>
<td>12.4</td>
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<td>10</td>
<td>13.5</td>
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<tr>
<td>20</td>
<td>15.8</td>
<td>22.0</td>
<td>22.0</td>
</tr>
<tr>
<td>Lattice Strain</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2.9</td>
<td>2.3</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Average particle size Dₘₐₑₙ (nm)</td>
<td>350±0.07, 336±0.39, 387±0.18, 351±0.13</td>
<td>567±0.17, 502±0.08, 557±0.03, 552±0.11</td>
<td></td>
</tr>
<tr>
<td>Theoretical density (g/cm³)</td>
<td>15.3</td>
<td>15.3</td>
<td>15.3</td>
</tr>
<tr>
<td>Pycnometer density (g/cm³)</td>
<td>13.9±0.01</td>
<td>13.2±0.02</td>
<td>13.0±0.01</td>
</tr>
</tbody>
</table>

Figure 3. XRD patterns of the WB-x wt.% WSi₂ (x=0, 5, 10 and 20) bulk products sintered from the (a) dry milled powders and (b) wet milled powders.
OM images of the dry/wet milled and sintered products are demonstrated in Figure 4(a)-(h). Generally, it can be seen from the OM images that the phase distributions in the microstructure were improved by changing WSi₂ amounts. In the OM image of dry milled WB without any WSi₂ addition (Figure 4(a)), some segregations were observed in the microstructure. Increasing the amount of WSi₂ prevented the formation of these segregations and assisted to provide homogeneous distributions. (Figure 4(a)-(d)). In addition, the wet milled products (Figure 4(e)-(h)) had more homogeneous phase dispersion than those of dry milled ones (Figure 4(a)-(d)). Also, further WSi₂ addition reduced the particle sizes of the existing phases due to its brittle character for both milling conditions.

Green density of the compacted samples, Archimedes density and Vickers microhardness of the sintered products are given in Table 3. The green density values of the compacted samples increased approximately 15% after sintering, indicating that the sintering process did not provide full densification. The Archimedes density and Vickers microhardness values of the products fluctuated according to the changing composition and milling atmosphere. There is no correlation between the increasing WSi₂ amount and property improvement, excepting 20 wt.% WSi₂ added samples. However, the Archimedes density and Vickers microhardness values of the products showed consistency with each other. The highest Archimedes density and Vickers microhardness values were belonged to the dry milled and sintered WB-20 wt.% WSi₂ sample. Even though the densities of dry milled and sintered WB-0 wt.% WSi₂ and WB-20 wt.% WSi₂ samples were similar, the addition of 20 wt.% WSi₂ resulted in a hardness difference about 4.55 GPa. Amongst the wet milled products, the highest density and microhardness were obtained in the WB-20 wt.% WSi₂ sample. However, the XRD patterns of the wet milled and sintered products pointed out the presence of ZrO₂ (Figure 3(b)). Existing undesired ZrO₂ contamination negatively affected the density values whose theoretical density values were calculated according to the WB and WSi₂ phases without taking into account the W₂B and ZrO₂ phases. In this content, the decrease in the density of dry milled products with increasing WSi₂ content.

![Figure 4. OM images of the WB-x wt.% WSi₂ bulk products sintered from the dry milled powders [(a) x=0, (b) x=5, (c) x=10, (d) x=20], and wet milled powders [(e) x=0, (f) x=5, (g) x=10, (h) x=20].](image)

<table>
<thead>
<tr>
<th>Amount of WSi₂ (wt.%)</th>
<th>Green Density (%)</th>
<th>Archimedes Density (%)</th>
<th>Vickers Microhardness, (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry milling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>67.2</td>
<td>90.5</td>
<td>8.85±2.4</td>
</tr>
<tr>
<td>5</td>
<td>67.1</td>
<td>81.7</td>
<td>8.96±2.1</td>
</tr>
<tr>
<td>10</td>
<td>70.3</td>
<td>83.8</td>
<td>8.34±1.9</td>
</tr>
<tr>
<td>20</td>
<td>81.2</td>
<td>90.7</td>
<td>13.36±2.8</td>
</tr>
<tr>
<td>Wet milling</td>
<td></td>
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<tr>
<td>0</td>
<td>55.4</td>
<td>78.5</td>
<td>10.42±1.7</td>
</tr>
<tr>
<td>5</td>
<td>57.9</td>
<td>80.5</td>
<td>6.78±1.9</td>
</tr>
<tr>
<td>10</td>
<td>48.6</td>
<td>76.2</td>
<td>5.79±0.7</td>
</tr>
<tr>
<td>20</td>
<td>62.6</td>
<td>86.9</td>
<td>11.54±2.7</td>
</tr>
</tbody>
</table>
could be related with the undetected ZrO$_2$. Chen et al. showed that the denseness of WB had an obvious effect on hardness, and fully dense WB product fabricated by an ultrahigh-pressure hot-press had an average hardness value of 28.9±0.8 GPa [30]. The different hardness values between the literature and this study can be attributed to the addition of WSi$_2$ phase, the formation of W$_2$B second phase, the emergence of ZrO$_2$ contamination and the lower density values of the sintered products caused by a different sintering method.

The SEM images taken from the fractured surfaces of the dry/wet milled and sintered products with the addition of 0, 10 and 20 wt.% WSi$_2$ are given in Figure 5(a)-(f). SEM micrographs showed that the addition of WSi$_2$ did not impair the densification mechanism of WB, in contrast with the Archimedes densities below 20 wt.% WSi$_2$ content (Table 3). According to SEM images, the average grain sizes were around 1-3 µm which indicated that a grain coarsening occurred during sintering. There were no significant change with increasing WSi$_2$ content in terms of grain size and morphologies of the sintered products. The presence of ZrO$_2$ contamination could not be detected from the fractured surfaces of the wet milled and sintered products. In order to detect the ZrO$_2$ contamination more clearly in the wet milled and sintered samples, SEM analyses were also conducted on the surfaces of the as-sintered samples. The representative SEM and EDS analyses of the wet milled and sintered WB-10 wt.% WSi$_2$ sample are illustrated in Figure 6(a) and (b), respectively. Figure 6(a) showed grains smaller than 5 µm. The EDS analysis of the red-marked region in Figure 6(a) pointed out that there was ZrO$_2$ contamination located between the grain boundaries. According to the general EDS result taken from whole sample surface, the detected amount of Zr was about 2 wt.%. However, Zr content in the red-marked area was determined as 58 wt.%. These results also indicated that the presence of ZrO$_2$ caused a low grain boundary diffusion rate and created a precipitation formation located at the grain boundaries which inhibited full densification [31].

3.3. Oxidation stabilities of the sintered products

In order to investigate oxidation stabilities of the composites, cold pressed and sintered samples were subjected to thermogravimetric analyses. Figure 7(a)-(d) indicates the weight change versus time plots of the dry/wet milled and sintered products during isothermal oxidation at 500 and 1000 °C. It can be clearly stated that the addition of WSi$_2$ content had a positive effect on the oxidation behavior of WB. Continuous weight gain with time was observed at 500 °C for all samples. Moreover, the weight gain got a similar rate with increasing WSi$_2$ content for both milling types in Figure 7(a) and (b). Wet milled samples exhibited slightly higher weight gaining at 500 °C than those of dry milled samples. As obviously seen in Figure 7(c) and (d), dry milling contributed to the oxidation stabilities of the samples comparing to the wet milling at 1000 °C. For this temperature, the weight gains suddenly accelerated after oxidation duration of 30 min and it slowed down after about 60 min. Although WB sample without WSi$_2$ addition showed the same oxidation curve for both milling types in Figure 7(c) and (d), the addition of WSi$_2$ content was found more effective for dry milling at 1000 °C, as similar to the behaviors at 500 °C. Thus, it can be said that the contribution of WSi$_2$ addition on the oxidation stability of WB was higher for dry milled samples at low and high temperatures than those of wet milled ones.

![Figure 5. SEM images taken from fractured surfaces of the WB-x wt.% WSi$_2$ bulk products sintered from the dry milled powders [(a) x=0, (b) x=10 and (c) x=20] and wet milled powders [(d) x=0, (e) x=10 and (f) x=20].](image-url)
4. Conclusion

In this study, WB-x wt.% WSi₂ (x=0, 5, 10 and 20) composites were fabricated by dry or wet milling, cold isostatic pressing and pressureless sintering. The sintered products consisted of WB, W₂B and WSi₂ phases. The XRD and SEM/EDS studies revealed that wet milled and sintered samples contained a small amount

Consequently, the addition of WSi₂ into the WB matrix improved the density and microhardness values after a particular amount whereas WSi₂ positively contributed to the oxidation behavior of tungsten borides for its all amounts. This study may lead for further investigations related with the transition metal borides, considering the improvements in the properties of tungsten borides.
of ZrO₂ contamination released from milling media. Although the density and microhardness values of the samples were not obtained as high as expected, they were in good correlation with each other. Oxidation tests showed that the addition of WSi₂ phase enhanced the oxidation stability of composites both under low and high temperatures. Comparing dry and wet milling processes prior to the sintering, it can be stated that their oxidation behaviors did not differ from each other at 500 °C. However, dry milling was more effective in the oxidation stabilities of the composites at 1000 °C. The best density (90.7 %), microhardness (13.36±2.8 GPa) and oxidation stability results amongst the fabricated composites were obtained for the dry milled and sintered WB-20 wt.% WSi₂ sample.

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References


