HfB$_2$/SiC Composite Consolidated by Spark Plasma Sintering

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Abstract

The stacking disordered SiC synthesized by mechanical alloying (MA) of Si and C powders was mixed with HfB$_2$ powder in a volume ratio of HfB$_2$/SiC=80/20 and subsequently the mixed powders were consolidated by spark plasma sintering at 1900°C without additives. The relative density of the composite reached 99.1%, which was higher than that in the usage of commercial SiC with HfB$_2$, 96.0%. The consolidation of the composite was accelerated by MA-SiC and the maximum shrinkage rate in the consolidation process was also higher than the other. The grain size of the HfB$_2$/MA-SiC composite was approximately 1.5μm and smaller compared to the HfB$_2$/commercial-SiC composite.

Keywords: HfB$_2$; SiC; composite; consolidation; SPS

1. Introduction

Hafnium diboride (HfB$_2$) is a promising material for use in high temperature applications, such as sharp leading edges on future generations of reentry space vehicles, because of its high melting point and relatively good oxidation resistance. However, the improvement of those properties is still required, because the protection of the vehicles from aerodynamic heating is extremely important and difficult [1]. The endeavor for advancing those properties of HfB$_2$ has been carried out by many researchers, and it has been attempted by combining silicon carbide (SiC) as a second phase. The SiC addition improves not only the oxidation resistance of HfB$_2$ but also its mechanical property [2]. Although conventionally sintering additives and/or high temperature are often induce the coarsening of the microstructure and the decrease in the mechanical properties at high temperature, yet those sintering conditions are required to achieve the full density of composite because of low sinterability of HfB$_2$ and SiC from strong covalent bonding [3,4].

Recently, the authors reported an innovative consolidation method for SiC via mechanical alloying-spark plasma sintering (MA-SPS) technique [5]. With this technique, stacking disordered SiC was prepared from the elements by high-energy ball milling and then consolidated by SPS. Without additives, highly dense SiC (up to 99% relative density) was successfully obtained at 1900°C under a pressure of 70MPa. Also, the drastic density increase and the ordering of the stacking disordered structure to β-SiC were observed simultaneously in the temperature range from 1700 to 1800°C. The same method was applied to BN, C and BN/SiC system. In all cases, the improvement on their sinterability by MA-SPS method was observed with structural ordering.

In this research, mechanical alloyed SiC (MA-SiC) powder was mixed with HfB$_2$ and consolidated without additives by SPS. To discuss the influence of MA-SiC on sintering behavior of the composite, commercial SiC powder was selected for a comparison. Also, the mechanical properties of the composite consisted of different SiC were measured.
2. Experimental Procedure

MA-SiC powder was prepared by the same condition as our presented study and ball-milled for 24h to mix with HfB2 powder (-325mesh, 99.5% pure, CERAC Inc., USA) in the volume ratio of HfB2/SiC=80/20[5]. The mixed powders were consolidated under vacuum in a SPS apparatus (Model 1050, SPS Syntex Co., Japan). The mixed powders were placed into a cylindrical graphite die. A pressure of 100MPa was then applied through top and bottom punches. The samples were then heated at a rate of about 100°C/min up to the desired temperature, which ranged from 1500 to 1900°C. For comparison, we selected commercial SiC powder (ca. 0.3μm, 99.5% pure, Betarundum, Iibden Co. Ltd., Japan). Commercial SiC was also consolidated with same condition of MA-SiC. The bulk density and the theoretical density were evaluated using the Archimedes’ method (water as immersing medium) and the rule-of-mixture, respectively. The relative density was calculated dividing the bulk density by the theoretical density (3.25 g/cm³ for SiC and 11.17g/cm³ for HfB2). The phase composition was analyzed with an X-ray diffractometer (XRD: RIGAKU RINT 2500, Rigaku Co., Ltd., Japan) and a scanning electron microscope (SEM: JSM-5400, JEOL, Japan) combined with an energy dispersive X-ray micranalyzer (EDS: JSM-5400, JEOL, Japan). Specimens were machined to 24×4×5 mm and polished for a 3-point bending strength measurement (PL-300, Marubishikagaku, Japan). The span length and crossed speed were 18mm and 0.2mm/min, respectively. The strength data were calculated based on the average of three measurements. The hardness was measured by Vickers method (HMV-2000, Shimazu, Japan) with a load of 98N and a holding time of 15s. The results of 10 measurements were averaged and used for the hardness data.

Results and Discussion

3.1. Shrinkage rate and density

Figure 1 shows the temperature and the shrinkage rate profiles during SPS of HfB₂, the HfB₂/C-SiC (the composite of HfB₂ and commercial SiC) and the HfB₂/MA-SiC (the composite of HfB₂ and MA-SiC). The shrinkage rate was defined as d(ΔL/L₀)/dt with L₀ as the thickness of the sample at room temperature. The shrinkage rate of pure HfB₂ increased around 1500°C. In contrast, the shrinkage rate of the HfB₂/MA-SiC and the HfB₂/C-SiC was larger than that of the pure HfB₂ over 1200°C. The onset of shrinkage of HfB₂ with SiC occurred at lower temperature than that of pure HfB₂. Over 1400°C, the onset of large shrinkage rate of the HfB₂/MA-SiC was observed compared with the HfB₂/C-SiC. The difference of shrinkage rate, which caused by the SiC variation, became larger with increasing in temperature and it took a maximum when the temperature reached around 1800°C.

![Fig. 1. Temperature and shrinkage rate profiles during SPS of HfB₂, HfB₂/C-SiC and HfB₂/MA-SiC.](image)

Fig. 1. Temperature and shrinkage rate profiles during SPS of HfB₂, HfB₂/C-SiC and HfB₂/MA-SiC.

![Fig. 2. The effect of sintering temperature on the relative density of HfB₂/MA-SiC and HfB₂/SiC.](image)

Fig. 2. The effect of sintering temperature on the relative density of HfB₂/MA-SiC and HfB₂/SiC.
Table 1 The mechanical properties of HfB₂/MA-SiC and HfB₂/C-SiC composite sintered at 1900°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative density (%)</th>
<th>HfB₂ grain size (µm)</th>
<th>Hv (GPa)</th>
<th>Bending strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfB₂/MA-SiC</td>
<td>99.1</td>
<td>1.5</td>
<td>20 ± 0.7</td>
<td>538</td>
</tr>
<tr>
<td>HfB₂/C-SiC</td>
<td>96.0</td>
<td>2.6</td>
<td>21 ± 0.7</td>
<td>362</td>
</tr>
</tbody>
</table>

Figure 2 shows the effect of sintering temperature on the relative density of the composite. Those composites exhibited almost same relative density below 1600°C. In contrast, the density of the HfB₂/MA-SiC became larger than that of the HfB₂/C-SiC when the temperature reached 1700 °C and higher. At 1900°C, the HfB₂/MA-SiC and the HfB₂/C-SiC showed 99% and 96% of relative density, although the pure HfB₂ exhibited only 73%.

Recently, the researchers, who studied HfB₂/SiC and ZrB₂/SiC system, reported that oxidized surface layers on SiC react with the other oxide from Hf or Zr boride, and then promote formation of liquid phases assisting in the densification at lower temperatures [6, 7]. This mechanism explains the phenomenon, which the shrinkage rate of the HfB₂/MA-SiC and the HfB₂/C-SiC over 1200°C and the final densities at 1900°C were larger than that of the HfB₂. However, the influence of the crystal structures of SiC on the shrinkage rate and the relative density over 1700°C is not clear.

To understand this issue, the difference in the crystal structure of SiC is an important key. The MA-SiC exhibited the stacking disordered structure before the consolidation process, and became β-SiC at 1900°C through structural ordering process. In contrast, C-SiC kept β-SiC as the original structure during the entire process. Those phenomena were observed by XRD in this research. Chatterjee et al. reported that the atomic diffusivities of Si and C in disordered SiC are larger than that in β-SiC [8]. In other words, the atomic diffusivities of MA-SiC are possibly larger than those of C-SiC. The atomic diffusion plays an important role in a consolidation. During the consolidation process, the large atomic diffusivity of SiC promoted the re-arrangement of HfB₂ and SiC grain and the mass transfer for the sintering of SiC at the lower temperature. Therefore, the difference of the shrinkage rate and the relative density on HfB₂/MA-SiC and the HfB₂/C-SiC became clear over 1700°C, which was the same temperature range as the onset of the drastic consolidation of the pure MA-SiC system [9].

3.2. Microstructure

Figure 3 shows SEM micrographs of the polished sections from HfB₂/MA-SiC composite and HfB₂/C-SiC sintered at 1900°C. The gray phase was HfB₂ and the dark phase was SiC. The average size of HfB₂ grains in HfB₂/C-SiC was 2.6µm, while that of HfB₂/MA-SiC was 1.5µm. As the result of comparison between both composites, the former composite showed SiC grains with finer size and better dispersion in HfB₂ matrix. Those results were confirmed in BEI and EDS.
of the average particle size of the starting SiC powder on controlling the final microstructure of the sintered composites, including controlling the HfB₂ grain size, was reported [10]. Because the particle size of MA-SiC powder is smaller than that of C-SiC powder, HfB₂/MA-SiC had prevented grain growth of the HfB₂ compared with HfB₂/C-SiC.

3.3. Mechanical properties

Table 1 shows the mechanical properties of the composite sintered at 1900°C. The hardness of the both composites was almost the same. On the other hand, the strength of the HfB₂/MA-SiC was 538MPa and higher than that of the HfB₂/C-SiC (362MPa). The other HfB₂/SiC, which hot-pressed without additives at 2100°C exhibited the bending strength of 590±50MPa [2].

In ZrB₂/SiC system, the hardness and the strength increased with fining size of SiC particle and improving its dispersion [10]. The both of HfB₂/MA-SiC and HfB₂/C-SiC exhibited similar hardness. However, the bending strength of the HfB₂/MA-SiC had larger than that of HfB₂/C-SiC. This could be attributed to better distribution and fine size of SiC particles in the former composite.

4. Conclusions

The stacking disordered SiC synthesized by mechanical alloying of Si and C powders was mixed with HfB₂ powder in a volume ratio of HfB₂/SiC=80/20 and subsequently the mixed powders were consolidated by SPS without additives. The relative density of HfB₂/MA-SiC composite was 99%, which was higher than that of HfB₂/C-SiC (96%) and HfB₂ (73%) at 1900°C. And, the conventional effect of SiC addition on the consolidation of the composite was obtained. In contrast, the clear influence of the crystal structures of SiC on the shrinkage rate and the relative density was observed over 1700°C, because the atomic diffusivities of MA-SiC are possibly larger than those of C-SiC, which can accelerate the re-arrangement of the grain and the mass transfer for the sintering of SiC at the lower temperature. The average size of HfB₂ grains in HfB₂/ MA-SiC composite (1.5μm) was smaller than that of HfB₂/commercial-SiC (2.6μm). The MA-SiC powders reduced grain growth of the HfB₂ phase. Also, the strength of HfB₂/MA-SiC was 538MPa which was higher than that of HfB₂/C-SiC (362MPa). It was attributed to better distribution and fine size of SiC particles.

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References