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RESEARCH ARTICLE

Preparation and mechanical properties of ZrB_2-based ceramics using $MoSi_2$ as sintering aids

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Abstract ZrB_2 (zirconium diboride)-based ceramics reinforced by 15vol.% SiC whiskers with high density were successfully prepared using $MoSi_2$ as sintering aids. The effects of sintering condition and $MoSi_2$ content on densification behavior, phase composition, and mechanical properties of SiC_w/ZrB_2 composites were studied. Nearly, fully dense materials (relative density > 99%) were obtained by hot-pressing (HP) at 1700°C–1800°C in flow argon atmosphere. The grain size of ZrB_2 phase in the samples sintered by HP at 1700°C–1800°C were very fine, with mean size below 5 μm. Mechanical properties (such as flexural strength, fracture toughness, and Vickers hardness) of the sintered samples were measured. The sample with 15vol.% $MoSi_2$ addition sintered by HP at 1750°C displayed the best mechanical properties.

Keywords zirconium diboride (ZrB_2), $MoSi_2$, sintering aids, mechanical properties

1 Introduction

Zirconium diboride (ZrB_2) ceramics have been widely studied due to their combination of physical properties, such as high melting temperature (3245°C), high strength, high electrical and thermal conductivity, chemical inertness against molten metals of nonbasic slags, and super thermal shock resistance [1,2]. These properties make them currently considered as ultra-high temperature ceramics (UHTCs). However, there are three main barriers limiting the application development of ZrB_2-based ceramics: relatively poor mechanical properties including low strength and fracture toughness, poor intrinsic sinterability because of the strong covalent bonds between Zr and B, and the poor oxidation resistance at high temperature.

A lot of studies have been done in order to address the barriers limiting the application development of ZrB_2-based ceramics. To improve the strength and fracture toughness of ZrB_2 ceramics, SiC particles [3], SiC whiskers [4,5], or carbon fibers [6] were used as reinforcements. However, a large amount of reinforcements will inhibit the sintering densification of ZrB_2 ceramics, which affects the mechanical properties of the ceramics. To improve the sintering densification of ZrB_2, very high sintering temperatures (2100°C–2300°C), pressure-assisted sintering procedures, and sintering additives are usually adopted. So far, a lot of metals (e.g., Cr and Fe) and ceramic powders (e.g., Si_3N_4, AlN, WC, and $MoSi_2$) were used to promote the sinterability of ZrB_2 [7–11]. $MoSi_2$ was found to be an effective additive to improve both sinterability and oxidation resistance of ZrB_2 ceramics [12–14].

In this study, $MoSi_2$ was selected as sintering aids, and SiC whisker was selected as toughness phase. The aim of this work is to study preparation and properties of the composites in the system ZrB_2-15vol.% SiC whisker-(10vol.%–20vol.%) $MoSi_2$. The densification behavior, phase composition, mechanical properties, and microstructure of sintered materials were investigated.

2 Experimental procedures

Commercial powders were used to prepare the ceramic materials: ZrB_2 (purity ~95% with ZrO_2 as main impurity, mean particle size ~6.7 μm, China), nano-SiC whiskers (SiC_w, β-type, 99.5% pure, mean diameter < 100 nm,

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aspect ratio > 10, China), and $MoSi_2$ (purity ~95% with SiO_2 as main impurity, mean particle size ~6 μm, China). The preparation processing of the ZrB_2-based ceramics was described as follows: First, nano-SiC whiskers was dispersed in ethanol by ultrasonic dispersion for 15 min and then mixed with ZrB_2 powder and $MoSi_2$ powder at the given composition ratios in ethanol by ball-milling for 2 h using planetary ball milling with agate balls. The obtained slurry were leached and then dried. After drying, the powder was put into a graphite die coated with BN slurry. Then, the graphite die were placed into the furnace, and sintering was conducted by both hot pressing (HP). To investigate the effect of $MoSi_2$ content on properties of the ZrB_2-based ceramics, samples with additions of 10vol.%, 15vol.%, and 20vol.% $MoSi_2$ were prepared. The compositions, sintering conditions and density were shown in Table 1.

The bulk densities of the sintered samples were measured by the Archimedes method. The phase compositions were identified by X-ray diffraction (D/MAX-2550V, Japan) with Cu Kα radiation at 40 kV and 30 mA. For bending strength measurement, the sintered samples were cut and ground into test bars with a dimension of 4 mm × 3 mm × 36 mm. Each bar was then polished with diamond pastes down to 1 μm on the side, which would experience tension stress during testing. The corners were rounded with a 15-mm diamond grinding wheel. The strength measurement was carried out with mechanical tester (Astron AG2000A) using a three-point bending method with a span of 30 mm and a crosshead speed of 0.5 mm/min. The fracture toughness was measured using the single edged notch beam (SENB) method with a crosshead speed of 0.05 mm/min and a span of 24 mm. The dimension of the test bars was 4 mm × 6 mm × 30 mm. For Vickers hardness measurement, each bar was polished with diamond pastes down to 0.5 μm on the side, which would experience pressure. The Vickers hardness measurement was carried out with a tester (HVS-50) under 100 N for 15 s. Each Vickers hardness value was calculated from at least five indentations. The microstructure of fracture surface was observed by scanning electron microscopy (SH-3000).

3 Results and discussion

3.1 Densification behavior

The measured bulk density values and the theoretical density values calculated from starting composition assuming no impurities and no reactions during sintering were summarized in Table 1.

From Table 1, all sintered samples had high bulk density. The relative densities of all samples were above 99%. For samples with 15vol.% $MoSi_2$ by hot pressing, relative density reached highest sintering at 1750°C, and it decreased as sintering temperature increased to 1800°C, which indicated that chemical reaction might happen during the sintering process. This reaction was proved by XRD results.

From the results, the sintering temperature of ZrB_2 reinforced by SiC_w could be reduced to 1700°C using $MoSi_2$ as additive by hot-pressing technique, which was much lower than 1950°C as reported by other researchers.

3.2 Phase composition

The XRD patterns of ZrB_2-based ceramics with 15vol.% $MoSi_2$ sintered at different temperature by hot-pressing technique were shown in Fig. 1.

In Fig. 1, when sintered at 1700°C, the diffraction peaks of ZrO_2 were observed besides those of ZrB_2, SiC, and $MoSi_2$. As sintering temperature increased, diffraction peaks of another phase emerged, identified as MoB. Diffraction peak intensities of MoB increased as sintering temperature increased. The existence of MoB indicated that chemical reaction happened between ZrB_2 and $MoSi_2$ during sintering process, which was also found in other researchers' studies [11,15]. The occurrence of MoB in samples at high sintering temperature may be the main reason for density decreasing.

The XRD patterns of ZrB_2-based ceramics sintered at 1750°C by hot-pressing technique with different content of $MoSi_2$ were shown in Fig. 2.

In Fig. 2, diffraction peaks of ZrO_2 were observed besides those of ZrB_2, SiC, and $MoSi_2$ in the patterns of all

Table 1 Summary of composition, sintering condition, and density

Label	Composition /vol.%	Sintering technique	Sintering condition	Theoretical density /(g·cm^{-3})	Bulk density /(g·cm^{-3})	Relative density /%
HP1	$ZrB_2 + 15SiC_w + 15MoSi_2$	hot pressing	1700°C/30 min/ argon/30 MPa	5.68	5.67±0.01	99.8
HP2	$ZrB_2 + 15SiC_w + 15MoSi_2$	hot pressing	1750°C/30 min/ argon/30 MPa	5.68	5.68±0.04	99.9
HP3	$ZrB_2 + 15SiC_w + 15MoSi_2$	hot pressing	1800°C/30 min/ argon/30 MPa	5.68	5.66±0.01	99.6
HP4	$ZrB_2 + 15SiC_w + 10MoSi_2$	hot pressing	1750°C/30 min/ argon/30 MPa	5.67	5.67±0.03	99.9
HP5	$ZrB_2 + 15SiC_w + 20MoSi_2$	hot pressing	1750°C/30 min/ argon/30 MPa	5.69	5.68±0.04	99.9

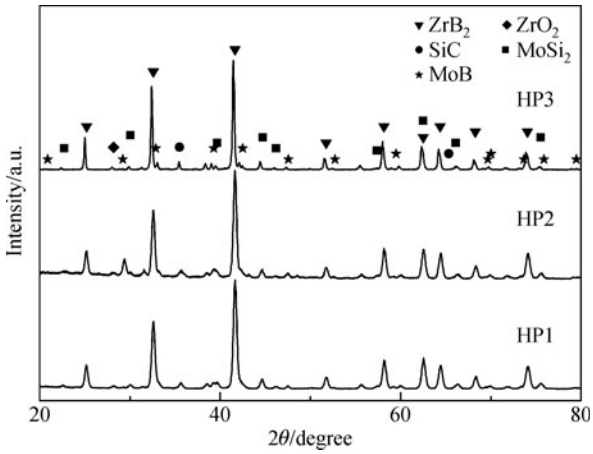

Fig. 1 XRD patterns of ZrB_2-based ceramics with 15vol.% $MoSi_2$ sintered at different temperatures by hot-pressing technique

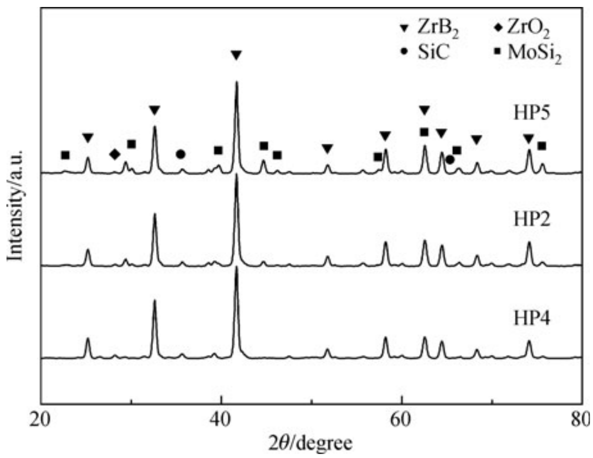

Fig. 2 XRD patterns of ZrB_2-based ceramics sintered at 1750°C by hot-pressing technique with different contents of $MoSi_2$

samples. As $MoSi_2$ content increased, diffraction peak intensities of $MoSi_2$ increased, while diffraction peak intensities of ZrO_2 decreased as $MoSi_2$ content increased. Except for those diffraction peaks of ZrB_2, SiC, $MoSi_2$, and ZrO_2, no other phase was found in all three samples.

As known to all, phase composition is one of the key factors influencing mechanical properties. Thus, the change of phase composition may result in change of mechanical properties.

3.3 Mechanical properties

Mechanical properties of ZrB_2-based ceramics with 15vol.% $MoSi_2$ sintered at different temperature by hot-pressing technique were shown in Table 2.

In Table 2, it could be seen that sintering temperature remarkably affected mechanical properties of the ZrB_2-based ceramics with 15vol.% $MoSi_2$ addition as sintering aids. The flexural strength of ZrB_2-based ceramics increased with increasing of sintering temperature and reached the maximum when sintering temperature was 1750°C. However, when sintering temperature was above 1750°C, the flexural strength decreased, which was related to the occurrence of MoB and the decline of bulk density. The effect of sintering temperature on fracture toughness was different from the case of flexural strength. The fracture toughness of the ZrB_2-based ceramics gradually increased with increasing sintering temperature and reached the maximum when sintering temperature was 1800°C. The fracture toughness of the sample sintered at 1750°C was close to that sintered at 1800°C. However, the Vickers hardness decreased with increasing sintering temperature. The Vickers hardness of the sample sintered at 1750°C was close to that at 1700°C. By comparing the above data, a conclusion could be drawn that the ZrB_2-based ceramics with 15vol.% $MoSi_2$ sintered at 1750°C possessed the best mechanical properties in this study.

Mechanical properties of the ZrB_2-based ceramics sintered at 1750°C by hot-pressing technique with different contents of $MoSi_2$ were shown in Table 3. In Table 3, it could be seen that $MoSi_2$ content affected the mechanical properties of the ZrB_2-based ceramics obviously. The flexural strength of the ZrB_2-based ceramics increased with the increase of $MoSi_2$ content and reached the maximum when $MoSi_2$ content was 15vol.%. However, when $MoSi_2$ content was above 15vol.%, flexural strength decreased. The effect of $MoSi_2$ content on the fracture toughness was similar to that of flexural strength. The fracture toughness of the ZrB_2-based ceramics obviously increased with the increase of $MoSi_2$ content and reached the maximum when $MoSi_2$ content was 15vol.%, but when $MoSi_2$ content was above 15vol.%, the fracture toughness decreased too. The fracture toughness of the sample with 15vol.% $MoSi_2$ was close to that with 20vol.%. Overall, the sample with 15vol.% $MoSi_2$ had the best mechanical properties.

3.4 Microstructure

Microstructure of the ZrB_2-based ceramics with 15vol.% $MoSi_2$ sintered at different temperatures by hot-pressing technique was observed by SEM, as shown in Fig. 3. In Fig. 3, there were few voids in the three samples sintered at different temperatures, which indicated that the relative densities of all the samples were high ($>99\%$). Thus, the addition of $MoSi_2$ was beneficial for the densification of the ZrB_2 ceramics. Compared Fig. 3(c) with 3(a) and 3(b), the voids in the sample sintered at 1800°C were much more than those of the samples sintered at 1700°C or 1750°C, which was consistent with the results of density measurement. The grain size of the three samples sintered at different temperatures was below 5 μm, which indicated that the addition of $MoSi_2$ was beneficial for hindering the growth of ZrB_2 grains. $MoSi_2$ phase could be accommodated among the ZrB_2 particles because of its ductility at temperatures over 1000°C [16], filling the voids left by the

Table 2 Mechanical properties of ZrB_2-based ceramics with 15vol.% $MoSi_2$ sintered at different temperatures by hot-pressing technique

Sintering temperature /°C	Flexural strength /MPa	Fracture toughness /(MPa·m$^{1/2}$)	Vicker hardness /GPa
1700	523.64±7.64	4.85±0.43	17.96±0.29
1750	564.72±11.21	5.52±0.03	17.64±0.15
1800	486.19±5.67	5.61±0.28	15.94±0.44

Table 3 Mechanical properties of ZrB_2-based ceramics sintered at 1750°C by hot-pressing technique with different contents of $MoSi_2$

Content of $MoSi_2$ /vol.%	Flexural strength /MPa	Fracture toughness /(MPa·m$^{1/2}$)
10	533.64±23.67	4.30±0.03
15	564.72±11.21	5.52±0.03
20	462.02±23.44	5.30±0.33

ZrB_2 skeleton, thus favoring the formation of a pore-free materials. The accommodation of $MoSi_2$ phase among ZrB_2 particles prevented diffusion of ZrB_2 during sintering, thus refined the grain size of the sintered samples. It could also be determined in Fig. 3 that intergranular fracture was the main fracture mode in the three ZrB_2 samples sintered at different temperatures.

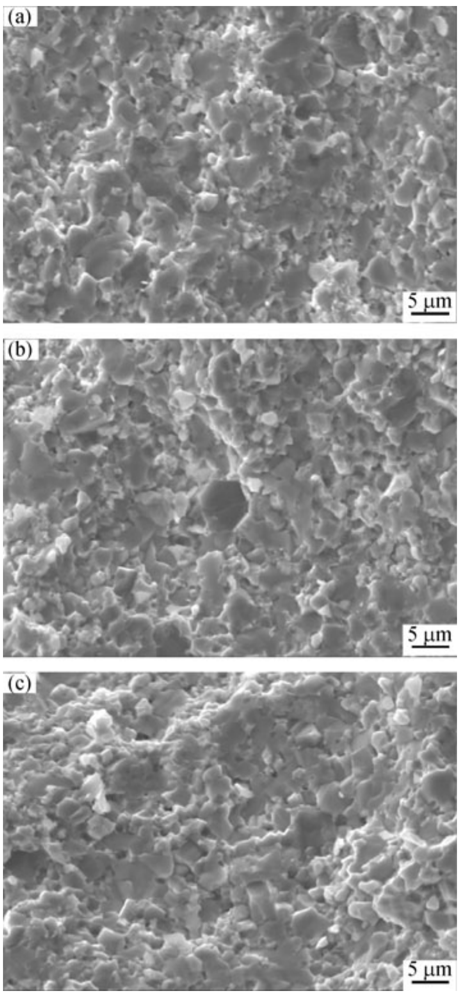

Fig. 3 Fractograph of the ZrB_2-based ceramics with 15vol.% $MoSi_2$ sintered at different temperatures by hot-pressing technique: **(a)** 1700°C; **(b)** 1750°C; **(c)**1800°C

High density, small grain size, and intergranular fracture were beneficial for mechanical properties of the ZrB_2-based ceramics, thus flexural strength and fracture toughness of the ZrB_2-based ceramics using $MoSi_2$ as sintering aids were 560 MPa and 5.5 MPa·m$^{1/2}$, respectively.

4 Conclusions

ZrB_2 ceramics toughened by 15vol.% SiC whisker with high density were successfully prepared using $MoSi_2$ as sintering aids by hot pressing. The flexural strength and fracture toughness of ZrB_2-15vol.% SiC whisker-15vol.% $MoSi_2$ ceramics sintered at 1750°C are 560 MPa and 5.5 MPa·m$^{1/2}$, respectively. It is revealed that the addition of $MoSi_2$ is beneficial for the densification and microstructure of ZrB_2-based ceramics.

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