Original Article

**Effect of MoSi₂ addition and particle size of SiC on pressureless sintering behavior and mechanical properties of ZrB₂–SiC–MoSi₂ composites**

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**A R T I C L E   I N F O**

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Article history:
Received 19 February 2015
Accepted 22 October 2015
Available online 23 November 2015

Keywords:
ZrB₂–SiC–MoSi₂ composites
Pressureless sintering
Microstructure
Mechanical properties
Oxidation resistance

**A B S T R A C T**

In the present paper, ZrB₂–SiC–MoSi₂ composites were prepared by pressureless sintering at temperatures of 2050, 2100 and 2150 °C for 1 h under argon atmosphere. In order to prepare composite samples, ZrB₂ powder was milled for 2 h, then the reinforcing particles including of micron and nano-sized SiC powder were added. MoSi₂ was added to ZrB₂ from 0 to 5 wt.% as sintering aid. The mixtures were formed and, after the pyrolysis, they were sintered. Densification, microstructure and mechanical properties of ZrB₂–SiC composites were investigated. The shrinkage of samples was measured, and the microstructure of samples was examined using scanning electron microscopy (SEM), equipped with EDS spectroscopy. In order to examine the oxidation behavior, the samples were heat treated at 1500 °C in air and then their weight changes were measured. Room temperature mechanical properties were examined. Mass fraction of MoSi₂, particle size of SiC powder and sintering temperature have a great effect on relative density, porosity, shrinkage, hardness, fracture toughness, oxidation resistance and microstructure of these composites. The highest relative density, hardness, fracture toughness and weight changes of 98.7%, 16.17 GPa, 3 MPa m¹/² and 0.28%, respectively, were obtained in ZrB₂–10 wt.%SiCnano–4 wt.%MoSi₂ composites sintered at 2150 °C.

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1. **Introduction**

ZrB₂ is one of the ultra high temperature ceramics (UHTCs) and is the most important candidate for a variety of high-temperature structural applications that require exposure to extreme thermal and chemical environments [1,2].

Densification of pure ZrB₂, because of its poor sinterability, is difficult and requires high temperatures and external pressure [3–6].

One of the most common additives used to improve not only ZrB₂ densification process by reacting with oxide impurities, but also the mechanical properties particularly the fracture toughness and oxidation resistance, is silicon carbide...
(SiC) [7–16]. Silicon carbide is added to ZrB2, producing the formation of a protective borosilicate glass at temperatures above 1200 °C that improves oxidation resistance of this ceramic material [17,18]. ZrB2 ceramics with SiC additions have typically been sintered by hot pressing [13] and recently spark plasma sintering [11]. Recently, it is found that pressureless sintering due to its low cost is one of the simplest methods to fabricate near-net shape ZrB2-based composites [8,19].

Sintering aids have been used to improve densification and decrease sintering temperature. In some research, MoSi2 has been used as sintering aid for the densification of ZrB2 by pressureless sintering [20–22] and pressure-assisted sintering [23–27].

In this study, ZrB2–SiC–MoSi2 composites were prepared by pressureless sintering. The sintering temperature, SiC particle size and MoSi2 content on densification behavior, mechanical properties, oxidation resistance and microstructure of the composites was investigated.

### 2. Experimental procedure

In the present paper, ZrB2–SiC–MoSi2 composites were produced by the pressureless sintering method and SiC powders in nano and micro-sized scale and MoSi2 powders in the range of 0–5 wt.% were used. According to earlier work [19] SiC powder in nano-sized (40 ± 10 nm) and micron-sized (1 ± 0.1 μm) were added in amount of 15 wt.% and 10 wt.%, respectively. In order to produce the composite samples, ZrB2 powder was first milled with ethanol and tungsten carbide balls for 2 h in a planetary ball mill. The ball-to-powder weight ratio and the rotational speed were defined 10:1 and 200 rpm respectively. Then nano-sized and micro-sized SiC particles and MoSi2 particles were added separately. The mixture was cold uniaxially pressed at 90 MPa inside a steel die with 10 mm diameter to form pellets with 5 mm height and then was pressed by CIP at 2000 bar (200 MPa) to increase the green compact’s strength. After preparation, the samples were pyrolyzed in an argon atmosphere at 1000 °C to remove resin. The pressureless sintering process was conducted under argon atmosphere at 2050 °C, 2100 °C and 2150 °C for 1 h. Table 1 shows the name and compositions of samples produced in this research.

In order to compare the effects of both nano and micro-sized SiC, as well as content of MoSi2 and processing conditions on pressureless sintering behavior of ZrB2–SiC–MoSi2 composite, the shrinkage percentage of samples was measured and the microstructure of the samples was examined using scanning electron microscopy (SEM), equipped with EDS spectroscopy. The bulk density of each of the sintered samples was evaluated by Archimedes principle. Relative densities were calculated by normalizing the measured bulk density by the corresponding theoretical density calculated using the rule of mixtures. The Vickers hardness and indentation fracture toughness were measured by using a Vickers hardness tester at the load of 20 kgf for 15 s. In order to evaluate oxidation resistance of the composites, the sintered samples were heated at 1500 °C for 30 min in air and then their weight changes were measured.

#### 3. Results and discussions

Fig. 1 shows the effect of MoSi2 content and particle size of SiC powders on relative density of ZrB2–SiC–MoSi2 composites sintered at different temperatures. In Fig. 2 porosity changes with MoSi2 addition and size of SiC particles at different temperatures can be observed. Fig. 3 shows the effect of MoSi2 addition and particle size of SiC powders on shrinkage of ZrB2–SiC composites sintered at 2050 °C. In Figs. 1 and 2 it can be observed that increasing the sintering temperature from 2050 °C to 2100 °C and 2150 °C results in a considerable increase in relative density and decrease in porosity. It can be confirmed that in sintering process, temperature acts as an important factor. The rapid increase in the shrinkage for ZrB2–SiC composites containing MoSi2 is attributed to the formation of a liquid phase. According to Eq. (1), in presence of MoSi2 the surface of ZrB2 particles reacts with impurities to form liquid phase of MoB. This helps to decrease porosity and increase the relative density, which improves densification [21,23–28].

\[
2\text{MoSi}_2 + 2\text{B}_2\text{O}_3 + \text{ZrO}_2 \rightarrow \text{ZrB}_2 + 4\text{SiO}_2 + 2\text{MoB}
\]  

(1)

In this equation, Gibbs free energy is −296 kJ at 25 °C and ambient pressure. The improved densification of

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition</th>
<th>Sintering temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZS15</td>
<td>ZrB2–15%SiC</td>
<td>205,021,002,150</td>
</tr>
<tr>
<td>ZSN10</td>
<td>ZrB2–10%SiCm</td>
<td>205,021,002,150</td>
</tr>
<tr>
<td>ZSM1</td>
<td>ZrB2–15%SiC–1%MoSi2</td>
<td>205,021,002,150</td>
</tr>
<tr>
<td>ZSM2</td>
<td>ZrB2–15%SiC–2%MoSi2</td>
<td>205,021,002,150</td>
</tr>
<tr>
<td>ZSM3</td>
<td>ZrB2–15%SiC–3%MoSi2</td>
<td>205,021,002,150</td>
</tr>
<tr>
<td>ZSM4</td>
<td>ZrB2–15%SiC–4%MoSi2</td>
<td>205,021,002,150</td>
</tr>
<tr>
<td>ZSM5</td>
<td>ZrB2–15%SiC–5%MoSi2</td>
<td>205,021,002,150</td>
</tr>
<tr>
<td>ZSMN1</td>
<td>ZrB2–10%SiCm–1%MoSi2</td>
<td>205,021,002,150</td>
</tr>
<tr>
<td>ZSMN2</td>
<td>ZrB2–10%SiCm–2%MoSi2</td>
<td>205,021,002,150</td>
</tr>
<tr>
<td>ZSMN3</td>
<td>ZrB2–10%SiCm–3%MoSi2</td>
<td>205,021,002,150</td>
</tr>
<tr>
<td>ZSMN4</td>
<td>ZrB2–10%SiCm–4%MoSi2</td>
<td>205,021,002,150</td>
</tr>
<tr>
<td>ZSMN5</td>
<td>ZrB2–10%SiCm–5%MoSi2</td>
<td>205,021,002,150</td>
</tr>
</tbody>
</table>
MoSi₂-containing ZrB₂–SiC composites is driven by a ZrB₂–MoB pseudo-binary reaction [23,28]. In this work it can be observed that by adding MoSi₂ up to 4 wt.% maximum relative density of 98.7% for composites containing nanosized SiC particles sintered at 2150 °C can be obtained and this relative density is more than which is reported at higher sintering temperature in [19].

Fig. 4 shows SEM micrographs of ZrB₂–SiC–MoSi₂ composites sintered at 2050 °C containing 15 wt.%SiCmicron and different amounts of MoSi₂. In this figure one can observe different areas with different colors, which gray, dark gray, light gray and black parts refer to matrix (ZrB₂), SiC, (Zr,W)C and porosity phases, respectively. It must be mentioned that tungsten carbide from the milling balls contaminates mixture and then reacts with zirconium to form (Zr,W)C during heat treatment. In this figure, porosity and grain size changes by MoSi₂ addition have been shown. It can be observed that adding MoSi₂ promotes densification by reducing porosities and the other hand makes the grains to grow by creating the liquid phase.

Figs. 5 and 6 show the effect of content of MoSi₂ and particle size of SiC on harness and fracture toughness of ZrB₂–SiC–MoSi₂ composites sintered at 2100 °C and 2150 °C. In these figures it is observed that by adding MoSi₂ up to 4 wt.%, both hardness and fracture toughness increase and then decrease. This can be related to decrease in porosity and then grain growth. As a consequence, a decrease occurs in the mechanical properties by adding MoSi₂ to the ZrB₂–SiC composites. In these figures, it is obvious that sintering temperature and size of SiC powder affect hardness and fracture toughness. Therefore, ZrB₂–10 wt.%SiCnano–4 wt.%MoSi₂ composite sintered at 2150 °C shows a maximum in hardness and fracture toughness of 16.17 GPa and 3 MPa m¹/², respectively. Guo et al. [24] obtained these values for hardness and fracture toughness for hot pressed ZrB₂–20 vol.%SiC–20 vol.%MoSi₂ composite, while in their work a relative density of 94.6% was obtained. Scitti et al. [20] obtained composites with microhardness of about 16 GPa by pressureless sintering method while in

Fig. 2 – The effect of content of MoSi₂ and particle size of SiC powders on porosity of ZrB₂–SiC–MoSi₂ composites sintered at different temperatures.

Fig. 3 – The effect of content of MoSi₂ and particle size of SiC powders on shrinkage of ZrB₂–SiC–MoSi₂ composites sintered at 2050 °C.

Fig. 4 – SEM micrographs of ZrB₂–SiC–MoSi₂ composites sintered at 2050 °C containing 15 wt.%SiCmicron and: (a) 1 wt.%MoSi₂; (b) 3 wt.%MoSi₂ and (c) 5 wt.%MoSi₂.
Fig. 5 – The effect of content of MoSi$_2$ and particle size of SiC powders on hardness of ZrB$_2$–SiC–MoSi$_2$ composites sintered at different temperatures.

Fig. 6 – The effect of content of MoSi$_2$ and particle size of SiC powders on fracture toughness of ZrB$_2$–SiC–MoSi$_2$ composites sintered at different temperatures.

their work fracture toughness was 2.3 MPa m$^{1/2}$. In an earlier research [19], ZrB$_2$–SiC composite containing 10 wt.% SiC in nano-sized sintered at 2200 °C for 60 min showed the highest value, i.e., 15.02 GPa. In the present work, by adding MoSi$_2$ in amount of 4 wt.% the obtained composite has higher hardness by sintering at lower temperature. Decrease in mechanical properties by adding more than 4 wt.% of MoSi$_2$ can be related to grain growth in matrix in presence of liquid phase. Fig. 7 shows SEM micrographs of ZrB$_2$–SiC–MoSi$_2$ composites sintered at 2100 °C containing different amount of MoSi$_2$ and SiC (micron and nano-sized). In this figure, it can be observed that, for composites containing micro and nano-sized SiC particles, by adding MoSi$_2$ up to 4 wt.%, a decrease in porosity occurs and, at the same time, grain growth is also observed. In comparison with composites containing micron-sized SiC, the nano-sized one has denser microstructure. According to other authors, the size of SiC particles has an important

Fig. 7 – SEM micrographs of ZrB$_2$–SiC–MoSi$_2$ composites sintered at 2100 °C containing: (a) 15 wt.%SiC$_{mic}$–0 wt.%MoSi$_2$; (b) 10 wt.%SiC$_{nano}$–0 wt.%MoSi$_2$; (c) 15 wt.%SiC$_{mic}$–2 wt.%MoSi$_2$; (d) 10 wt.%SiC$_{nano}$–2 wt.%MoSi$_2$; (e) 15 wt.%SiC$_{mic}$–4 wt.%MoSi$_2$; (f) 10 wt.%SiC$_{nano}$–4 wt.%MoSi$_2$; (g) 15 wt.%SiC$_{mic}$–5 wt.%MoSi$_2$ and (h) 10 wt.%SiC$_{nano}$–5 wt.%MoSi$_2$. 
Fig. 8 – The effect of content of MoSi2 and particle size of SiC powders on weight changes of ZrB2–SiC–MoSi2 composites sintered at different temperatures after oxidation at 1500 °C for 30 min.

4. Conclusions

- ZrB2–SiC–MoSi2 composites were prepared by pressureless sintering at 2050–2150 °C for 60 min. In this work by adding MoSi2 particles to ZrB2–SiC composites, increasing sintering temperature and decreasing the particle size of SiC powder, densification and mechanical properties were improved. The mechanical properties and sintering behavior of the composites containing MoSi2 particles were much higher than those of ZrB2–SiC composites.

- Addition of MoSi2 up to 4 wt.%, improved the densification of ZrB2–SiC composites. ZrB2–10 wt.%SiCnano–4 wt.%MoSi2 composite sintered at 2150 °C for 60 min reached a maximum relative density of 98.7%.

- Vickers hardness and fracture toughness of ZrB2–SiC composites were increased by adding MoSi2 up to 4 wt.%.

ZrB2–10 wt.%SiCnano–4 wt.%MoSi2 composite sintered at 2150 °C for 60 min showed the highest values for hardness and fracture toughness, i.e., 16.17 GPa and 3 MPa m1/2, respectively.

- By adding MoSi2 up to 4 wt.% to ZrB2–SiC composites oxidation resistance can be improved. ZrB2–10 wt.%SiCnano–4 wt.%MoSi2 composite sintered at 2150 °C for 60 min showed the minimum weight changes of 0.28% after heating at 1500 °C for 30 min in air.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES