Original Article

Pressureless sintering behavior and mechanical properties of ZrB$_2$–SiC composites: effect of SiC content and particle size

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**Abstract**

In the present paper, ZrB$_2$–SiC composites were prepared by pressureless sintering at temperatures of 2000–2200 °C for 1 h under argon atmosphere. In order to prepare composite samples, ZrB$_2$ powder was milled for 2 h, then the reinforcing particles including of micron and nano-sized SiC powder were added. The mixtures were formed and, after the pyrolysis, they were sintered. Densification, microstructural and mechanical properties of ZrB$_2$–SiC composites were investigated. The shrinkage of samples was measured both before and after the sintering, and the microstructure of samples was examined using scanning electron microscopy (SEM), equipped with EDS spectroscopy. Both mass fraction and size of SiC powder have a great effect on relative density, porosity, shrinkage, hardness and microstructure of these composites. The highest relative density and hardness were 98.12% and 15.02 GPa, respectively, in ZrB$_2$–10 wt% SiC$_{nano}$ composite sintered at 2200 °C.

1. Introduction

ZrB$_2$ is one of the ultra high temperature ceramics (UHTCs) and is the most important candidate for applications that require exposure to extreme thermal and chemical environments such as aerospace applications [1,2]. Densification of pure ZrB$_2$ because of its poor sinterability is difficult and requires high temperatures with pressure [3–6].

Niihara and Nakahira [7] found that the mechanical properties of ceramics can be significantly improved by introducing nanosized ceramic particles into the ceramic matrix grains or grain boundaries. One of the commonest additives used to improve densification process by reacting with oxide impurities, mechanical properties particularly fracture toughness and oxidation resistance of ZrB$_2$ is silicon carbide (SiC) [8–17]. In ZrB$_2$–SiC composites, simultaneous oxidation of ZrB$_2$ and SiC results in a less volatile silica-rich surface, in place of the more volatile boria surface scale in the case of pure ZrB$_2$ [18,19]. The silica-rich surface scale is also more refractory and resistant to oxygen diffusion, making ZrB$_2$–SiC composites more oxidation resistant than pure ZrB$_2$. And also, the silica-rich scale is anchored by the oxidized sub-layer consisting of an interpenetrating composite of ZrO$_2$-silica glass.
ZrB₂–SiC materials have higher strength, fracture toughness than pure ZrB₂ [6,9,12]. Excellent mechanical properties have been attributed to maintaining a fine grain size and a uniform distribution of the reinforcing phase. ZrB₂ ceramics with SiC additions have typically been sintered by hot pressing [13,20] and recently spark plasma sintering [12,17]. 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 [8,9,15].

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

2. Experimental procedure

In the present paper, ZrB₂–SiC composites were produced by the pressureless sintering method and SiC powders at nano and micro-sized scale were used. 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 SiC and micro-sized SiC 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 (Cold Isostatic Press) at 2000 bar (200 MPa) to increase the green compact’s strength. After preparing the samples, they were pyrolyzed in an argon atmosphere at 1000 °C to remove resin as binder. The pressureless sintering process was conducted in the argon atmosphere at 2050 °C, 2100 °C, 2150 °C and 2200 °C for 1 h. Table 1 shows the name and compositions of samples produced in this research.

![Fig. 1](image1.png) **Fig. 1** – The effect of content and particle size of SiC powder on relative density of ZrB₂–SiC composites sintered at 2200 °C.

![Fig. 2](image2.png) **Fig. 2** – The effect of content and particle size of SiC powder on porosity of ZrB₂–SiC composites sintered at 2200 °C.

![Fig. 3](image3.png) **Fig. 3** – The effect of content and particle size of SiC powder on shrinkage of ZrB₂–SiC composites sintered at 2200 °C.

![Fig. 4](image4.png) **Fig. 4** – The effect of content and particle size of SiC powder on hardness of ZrB₂–SiC composites sintered at 2200 °C.
In order to compare the effects of nano and micro-sized SiC and processing conditions on pressureless sintering behavior of ZrB$_2$–SiC composite, the shrinkage percentage of samples was measured before and after sintering and the microstructure of the samples was examined using scanning electron microscopy (SEM; JEOL JSM-5800), equipped with EDS spectroscopy. Also, the matrix grain size was investigated with a Clemex image analyzer. The bulk density of each of the sintered samples was evaluated by Archimedes method. 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 (HM-221, Mitutoyo Corp.), at the load of 20 kgf for 15 s. The fracture toughness was calculated from the half-length of a crack formed around the indentations. The average value of the 20 measurements for each sample was used for the evaluations of hardness and toughness.

3. Results and discussion

In Figs. 1 and 2 the effect of SiC content and particle size on relative density and porosity of ZrB$_2$–SiC composites is shown respectively. It can be observed that by adding SiC to ZrB$_2$ up to 15 wt% (for micron-sized SiC powder) and 10 wt% (for nano-sized SiC powder) relative density increases and then decreases (Fig. 1). It can be concluded that SiC addition promotes densification and in the samples containing nano-sized SiC powder higher relative density can be obtained. Fig. 2 shows the decrease in porosity by increasing SiC content. Also in this figure, it is shown that decrease in SiC particle size promotes densification. Then introducing of SiC particles to ZrB$_2$ matrix up to 15 wt% and 10 wt% (for micron

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
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<td>2200</td>
<td>ZrB$_2$</td>
<td>Z$_2$</td>
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<tr>
<td>2200</td>
<td>ZrB$_2$–5 wt% SiC</td>
<td>ZS5</td>
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Fig. 6 – SEM micrographs of ZrB$_2$–SiC composites sintered at 2200 °C and containing different amount of micron-sized SiC powder: (a) 5 wt%; (b) 10 wt%; (c) 15 wt% and (d) 20 wt%.
and nano-sized SiC powder, respectively) results in increasing relative density and decreasing porosity [12,17,20]. It is found that densification of ZrB2 powder requires high temperatures, more than 2100 °C, because of the covalent character of the bonding and the low volume and grain boundaries diffusion rates. Commonly on the surfaces of the raw materials ZrB2 and SiC powder particles, B2O3 and SiO2 films are present, respectively. On the other hand, the presence of B2O3 on the surface of the raw materials inhibited densification in non-oxide ceramic system like ZrB2 because of evaporation of B2O3. Then, to modify sinterability of ZrB2, it is necessary to increase the diffusion rate and decrease the oxygen content and inhibit evaporation of B2O3 [21]. Improvement in densification due to the addition of SiC is related to the presence of an intergranular amorphous film of SiO2. This film prevents evaporation of B2O3 during sintering and leads to form a stable liquid phase among the grains, and then sinterability can be improved by liquid phase sintering mechanism [20]. It can be concluded that by adding SiC to ZrB2 ceramic, porosity of ZrB2–SiC system decreases and then its relative density increases. Introducing SiC more than 15 wt% and 10 wt% (for micron and nano-sized SiC powder, respectively) to ZrB2–SiC composites results in formation porous structures because of agglomeration of the fine particles [17].

In Fig. 3 the effect of content and particle size of SiC powders on shrinkage of ZrB2–SiC composites sintered at 2200 °C is shown. In this figure, it is shown that increasing SiC content and decreasing particle size of SiC powder lead to raising the shrinkage of sintering process. It is concluded that both adding SiC particles and decreasing particle size of SiC powder lead to improve densification.

In Fig. 4, the effect of SiC content and particle size on hardness of the samples sintered at 2200 °C is shown. In this figure, it can be observed that increasing SiC content up to 15 wt% and 10 wt% (for samples containing micron and nano-sized SiC particles, respectively) leads to a maximum hardness. This
increase in hardness by adding SiC particle to ZrB$_2$ matrix is related to higher hardness of SiC than ZrB$_2$ (HV$_\text{SiC}$ = 28 GPa and HV$_\text{ZrB}_2$ = 12 GPa). According to mixtures rule, adding a phase with higher hardness to a matrix with lower hardness makes composite to have higher hardness. In this figure, it can be observed that decrease in SiC particle size results in increasing the hardness. In the case of samples containing more than 15 wt% (micro particles) and 10 wt% (nano particles) decrease in hardness probably is due to agglomeration of SiC particles and formation of porous structure according to Fig. 2 [14,17]. It can be concluded that low hardness could be mostly due to inhomogeneous distribution and agglomeration of SiC particles.

Fig. 5 is a SEM micrograph of ZrB$_2$–5 wt% SiC$_\text{micron}$ composite sintered at 2200 °C. In this figure, there are some parts named as B, M, G and W and one can observe EDS results of these parts. According to EDS analysis B, M, G and W parts represent SiC, ZrB$_2$, (Zr, W)C and WC phases respectively. WC can be introduced through milling by WC balls and container. This inclusion reacts with ZrO$_2$ present on the surface of ZrB$_2$ fine particles to form (Zr, W)C solid solution [14] according to Eq. (1):

$$\text{ZrO}_2(s) + 3\text{WC}(s) \rightarrow \text{ZrC}(s) + 2\text{CO}(g) + 3\text{W}(s) \quad (1)$$

According to W–Zr–C phase diagram, formation of (Zr, W)C solid solution in this condition is confirmed. This solid solution is formed in grain boundaries and then acts as a grain growth inhibitor [22].

In Fig. 6 SEM micrographs of ZrB$_2$–SiC composites sintered at 2200 °C and containing different amount of micron-sized SiC powder are shown. In this figure, it can be observed that by increasing content of SiC up to 15 wt%, porosity decreases and then by adding of SiC more than 15 wt% porosity increases because of agglomeration of SiC particles. However, this figure confirms the results of porosity measurements. And also in Fig. 6 it can be observed that increasing the amount of SiC results in decreasing the grain size of matrix because SiC particles are placed in grain boundaries of ZrB$_2$ phase and act as inhibitor of grain growth during pressureless sintering [8,9,11].

Fig. 7 shows SEM micrograph of ZrB$_2$–SiC composites sintered at 2200 °C and containing different amount of nano-sized SiC powder. In this figure, it is shown that adding nano-sized SiC particles up to 10 wt% results in decreasing the porosity and then adding of SiC more than 10 wt% leads to increase the porosity because of agglomeration of nano-sized SiC particles.

Comparing Figs. 6 and 7 shows the effect of particle size of SiC particles on porosity of ZrB$_2$–SiC composites and grain size of matrix. It is concluded that decreasing size of SiC particles leads to decrease the porosity of ZrB$_2$–SiC composites and grain size of ZrB$_2$ matrix [8,9,11].

The effect of sintering temperature on relative density of ZrB$_2$–SiC composites containing different size of SiC particles is shown in Fig. 8. This figure shows that increasing sintering temperature results in increasing relative density. And also in this figure, it can be observed that decreasing the particle size of SiC powder leads to increase the relative density at lower temperatures while at higher temperatures the particle size is not too effective because at higher temperatures, the temperature plays an important role in densification. These results can be confirmed by Fig. 9. In this figure, the effect of sintering temperature and particle size of the second phase on porosity of composites is shown. According to Figs. 8 and 9 sintering temperature by activating diffusion mechanisms, improves densification and decreases the porosity. And also, it can be concluded that at higher temperatures particle size of SiC powder is not effective on decreasing the porosity. This is confirmed by the results of hardness measurements shown in Fig. 10. This figure shows the effect of sintering temperature and SiC particle size on hardness of ZrB$_2$–SiC composites. In this figure, it can be observed that increasing the sintering temperature leads to increase hardness because of decreasing porosity. And also, one can conclude that decreasing particle size of SiC powder by decreasing the grain size of matrix and porosity makes the composites containing nano-sized SiC particles to have higher hardness.

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**Fig. 8** – The effect of sintering temperature on relative density of ZrB$_2$–SiC composites.

**Fig. 9** – The effect of sintering temperature on porosity of ZrB$_2$–SiC composites.
Fig. 10 – The effect of sintering temperature on hardness of ZrB$_2$–SiC composites.

4. Conclusion

- ZrB$_2$–SiC composites were prepared by pressureless sintering at 2000–2200 °C for 60 min. In this work by adding nano-sized SiC particles to ZrB$_2$, densification and mechanical properties of ZrB$_2$–SiC composites were improved. The mechanical properties and sintering behavior of the obtained composites, were much higher than those of monolithic ZrB$_2$ and ZrB$_2$-based composites with micron-sized SiC particles.

- The addition of SiC up to 10 wt% and 15 wt% in nano-sized and micron-sized scales, respectively improved the densification of ZrB$_2$–SiC composites. The ZrB$_2$–SiC composites containing 10 wt% SiC in nano-sized and 15 wt% SiC in micron-sized scales, sintered at 2200 °C for 60 min reached a maximum relative density of more than 98% and 96%, respectively.

- Vickers hardness of ZrB$_2$–SiC composites were increased with increasing sintering temperature up to 2200 °C and SiC content up to 10 wt% and 15 wt% in nano-sized and micron-sized scales, respectively. The ZrB$_2$–SiC composites containing 10 wt% SiC in nano-sized and 15 wt% SiC in micron-sized scales, sintered at 2200 °C for 60 min showed the highest value, i.e., 15.02 GPa and 14.08 GPa, respectively.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES