

# Investigation on addition of $\text{ZrO}_2$ -3 mol% $\text{Y}_2\text{O}_3$ powder on sintering behavior and mechanical properties of $\text{B}_4\text{C}$

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**Abstract** The effect of  $\text{ZrO}_2$ -3%  $\text{Y}_2\text{O}_3$  addition on densification, sintering behavior and mechanical properties of a boron carbide matrix was investigated. When adding 0–30 wt% of  $\text{ZrO}_2$ -3%  $\text{Y}_2\text{O}_3$  to  $\text{B}_4\text{C}$  sintered densities were increased from 75% to 98.5%. Sinterability was significantly improved by addition of a small amount of  $\text{ZrO}_2$ -3%  $\text{Y}_2\text{O}_3$ . As a result of density improvement, mechanical properties such as hardness, strength and fracture toughness were increased remarkably. However, when the amount of  $\text{ZrO}_2$ -3%  $\text{Y}_2\text{O}_3$  exceed from 20 wt%. Hardness started to reduce.

## Introduction

The properties of boron carbide ( $\text{B}_4\text{C}$ ) ceramic such as hardness, resistance to abrasion, and low density makes it attractive for many industrial and strategic applications [1–19]. Its industrial uses include grinding wheels for sharpening cutting tools, super-abrasives in polishing and grinding media and fibers for reinforced ceramic composites. Because of its low specific gravity and high-resistance to piercing, it has also been used as a lightweight armor material [1–8]. However, their relatively low strength and fracture toughness have restricted wider applications as structural materials.

The main problem associated with the use of this material is its low sintering ability. In addition, since the low self-diffusivity does not allow densification by solid-state sintering techniques, metallic sintering aids such as Al [1], Si [2], Ti [3], Mg, and Fe are frequently added to provide a medium for liquid-phase sintering. However, metallic phases at the grain boundaries generally deteriorate the unique properties of hard ceramics. Nonoxide ceramics such as SiC [4–6], TiC [7], C [8],  $\text{W}_2\text{B}_5$  [9],  $\text{CrB}_2$  [10],  $\text{Be}_2\text{C}$  [11] and  $\text{TiB}_2$  [12–17] have also been found to be effective as sintering additives for  $\text{B}_4\text{C}$ . However, in these cases, either large amounts of second phase or high sintering temperatures are required for full densification. Even in presence of commonly used additives such as Mg, Al, C and  $\text{TiB}_2$ , boron carbide cannot be sintered at temperatures below 2000 °C.

It has been frequently observed that small amounts of oxides are very effective in improving the sinterability of nonoxide ceramics [18, 19]. According to the reports, Shorokhod et al. have been able to densify  $\text{B}_4\text{C}$ - $\text{TiB}_2$  composition to about 90% of theoretical density at 1900 °C [13]. However, for obtaining higher density above 90% it is necessary that sintering to be done at above 2200 °C. Few studies have been done regarding the use of transitional elements oxides such as  $\text{Cr}_2\text{O}_3$  [10] and  $\text{TiO}_2$  [3] to alleviate sintering temperature of  $\text{B}_4\text{C}$ . However, there have been a very limited number of studies using oxides as sintering aids for  $\text{B}_4\text{C}$ . The objective of the present study was to use yttria-stabilized zirconia (Y-PSZ) as the sintering aid to densify boron carbide powder at temperature up to 2150 °C.

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## Experimental

Boron carbide powder (Chengdu Rong feng china) having average particle size of 1  $\mu\text{m}$  and specific surface area of

14 m<sup>2</sup>/gr as the main raw material and ZrO<sub>2</sub>-3 wt%Y<sub>2</sub>O<sub>3</sub> (TOSOH) powder having average particle size of 0.8 μm and specific surface area of 16 m<sup>2</sup>/gr as the additive were used in this study. The ZrO<sub>2</sub> powder with mass fraction of 30% by weight was added to B<sub>4</sub>C powder and attrition milled for 8 hrs at 250 rpm in isopropyl alcohol. The green cylindrical samples were shaped using an uniaxial press under a pressure of 80 MPa.

The green samples sintered at 2050 °C and 2150 °C for 1 h under Ar atmosphere using a microprocessor controlled graphite element resistance furnace. The heating of B<sub>4</sub>C–ZrO<sub>2</sub> mixtures, under an argon atmosphere, generates B<sub>4</sub>C–ZrB<sub>2</sub> composites, because of a low temperature (<1500 °C) carbide–oxide reaction [19].

The density of the sintered samples was measured using Archimedes method [7, 13, 17, 19].

The hardness was measured according to Vickers micro hardness using a force of 1.96N [19, 20].

The bending samples having 3 × 4 × 45 mm<sup>3</sup> dimensions were cut from original sample by a precision cutter machine. The tensile side of the bending samples polished to a 1 μm surface finish. The corners of the samples were also lapped. The fracture toughness of the specimens was determined by the indentation strength method. The polished surface was indented at 98 N with a Vickers indenter for 15 s. The fracture strength was measured with the four-point flexural configuration [8, 15, 16, 18].

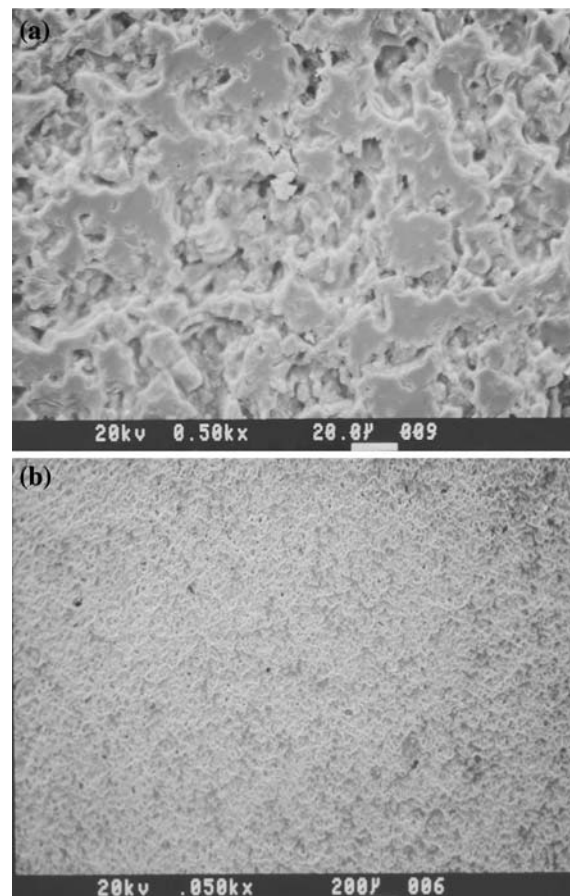
The microstructural examinations were performed using a scanning electron microscope (SEM). The samples, if needed, were electrically etched in 0.1% KOH solution with current density of 0.1 A/cm<sup>2</sup> for about 15 s.

## Result and discussion

Figure 1 shows SEM micrographs from the samples having 0–30% ZrO<sub>2</sub> sintered at 2050 °C for 1 h. As it can be seen, by increasing ZrO<sub>2</sub> not only the size of the grains reduces, but also the porosity reduces as well.

Figure 2 illustrates SEM micrographs of the same compositions sintered at 2150 °C for 1 hr. A comparison between Figs. 1a and 2a demonstrates that for pure B<sub>4</sub>C samples increasing the sintering temperature have no significant effect on porosity reduction. It is obvious that a grain coarsening has happened for the samples sintered at 2150 °C. Figure 3 shows the effect of ZrO<sub>2</sub> addition on relative density of the samples sintered at 2050 and 2150 °C. It can be seen that by increasing the ZrO<sub>2</sub> content the density increases. The higher amount of density obtained for a composition having 30 wt% in it.

It is also evident that by increasing the sintering temperature relative density increases.



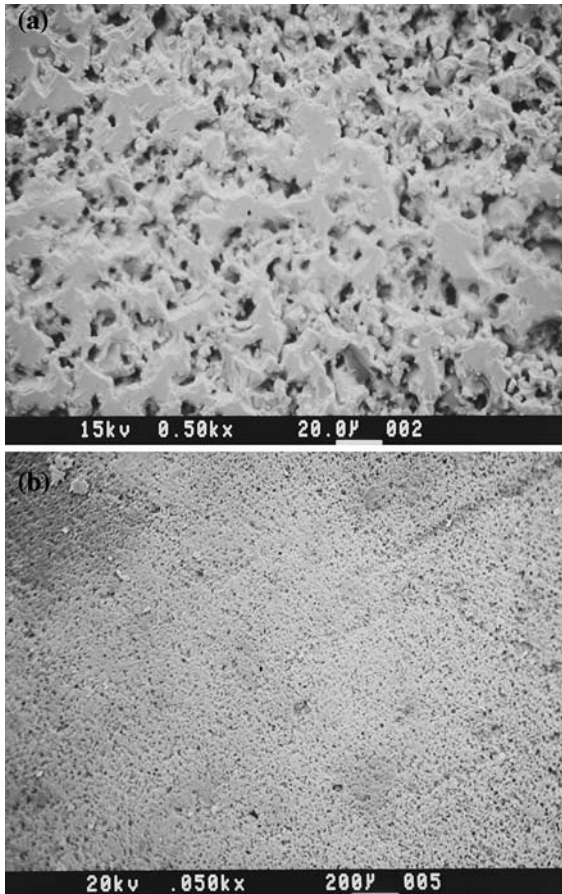
**Fig. 1** SEM micrographs of samples sintered at 2050 °C for 1 hr (a) B<sub>4</sub>C-free Zirconia (b) B<sub>4</sub>C-30% (ZrO<sub>2</sub>-3%Y<sub>2</sub>O<sub>3</sub>)

These results are in accordance with the microscopic examinations. It is evident that by addition of 15 wt% ZrO<sub>2</sub> and sintering at 2150 °C samples having 97% of theoretical density can be obtained. However, the densities of ZrO<sub>2</sub>-free samples were measured to be about 75% of theoretical density.

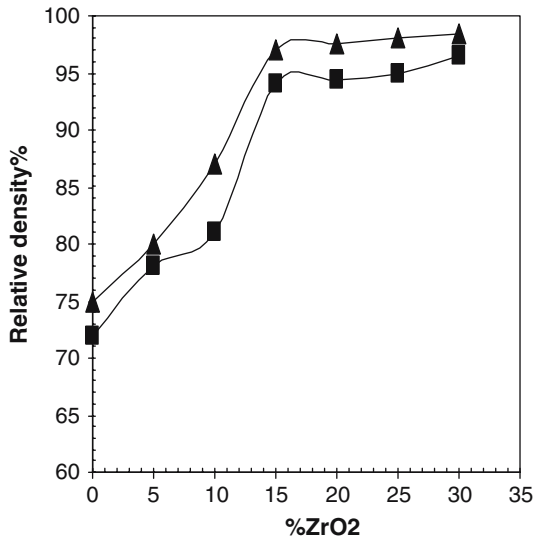
The addition of ZrO<sub>2</sub> has also a significant effect on mechanical properties of the samples. In Fig. 4 the hardness of the samples as a function of ZrO<sub>2</sub> percentage has been shown.

The figure shows that by addition of ZrO<sub>2</sub> up to 15 wt% the hardness increases and then starts to decrease by increasing the amount of ZrO<sub>2</sub>.

This is due to the formation of less hard ZrB<sub>2</sub> composition. Figure 5 demonstrates the effect of ZrO<sub>2</sub> addition on fracture toughness of the samples having 0–30 wt% ZrO<sub>2</sub> in their compositions. From the figure, it is obvious that by increasing the ZrO<sub>2</sub> content, the toughness of the samples increases. This can be related to the lower amount of porosity, high density, and also presence of ZrB<sub>2</sub> phase in the microstructure of such samples. The effect of ZrO<sub>2</sub>

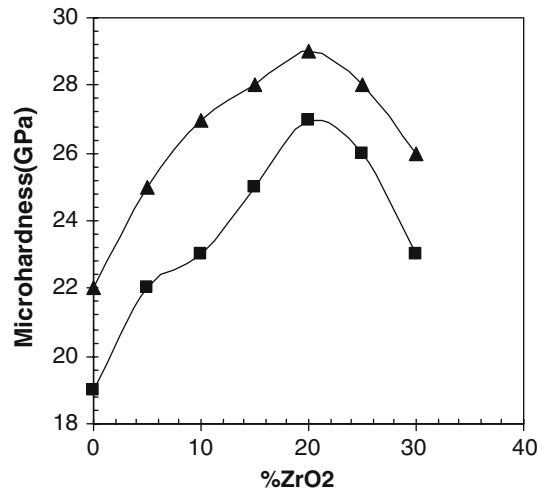


**Fig. 2** SEM micrographs of samples sintered at 2150 °C for 1 hr (a) B4C-free Zirconia (b) B4C-30% (ZrO<sub>2</sub>-3%Y<sub>2</sub>O<sub>3</sub>)

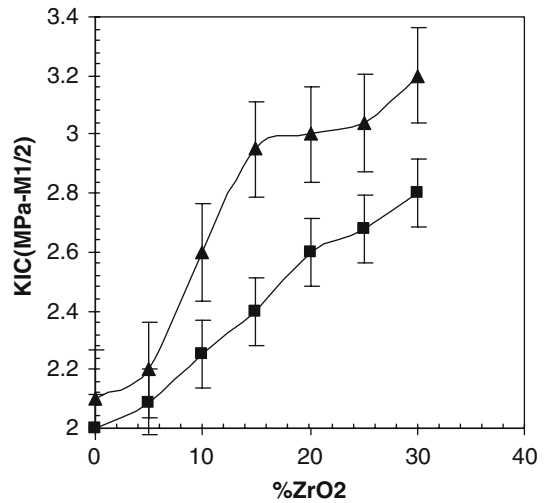


**Fig. 3** Effect of ZrO<sub>2</sub> addition on relative density of the samples sintered at 2050 °C (■) and 2150 °C (▲)

addition on bending strength of the specimens has been presented in Fig. 6 in which an increase in bending strength as a function of ZrO<sub>2</sub> percentage can be observed. The



**Fig. 4** Effect of ZrO<sub>2</sub> addition on Vickers Microhardness of the samples sintered at 2050 °C (■) and 2150 °C (▲)



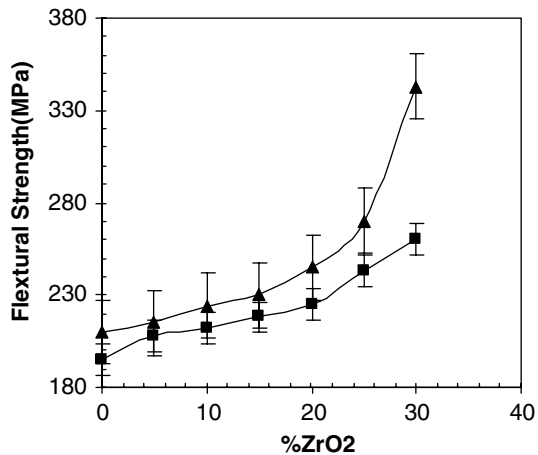
**Fig. 5** Effect of ZrO<sub>2</sub> addition on fracture toughness of the samples sintered at 2050 °C (■) and 2150 °C (▲)

same phenomenon affecting the toughness will control the strength as well.

### Conclusion

From the results of this study it can be concluded that:

1. Addition of ZrO<sub>2</sub> has remarkable effect on sintering and mechanical properties of B<sub>4</sub>C composition.
2. The optimum amount of ZrO<sub>2</sub> for improving the properties of B<sub>4</sub>C was found to be about 15 wt%. Addition of higher amount of ZrO<sub>2</sub> reduces the hardness of the samples.
3. Fracture toughness and bending strength increases by increasing the ZrO<sub>2</sub> addition up to 30 wt%. The effect of higher amount of ZrO<sub>2</sub> has not been studied yet.



**Fig. 6** Effect of ZrO<sub>2</sub> addition on flexural strength of the samples sintered at 2050 °C (■) and 2150 °C (▲).

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