

# Boron Carbide–Zirconium Boride *In Situ* Composites by the Reactive Pressureless Sintering of Boron Carbide–Zirconia Mixtures

The heating of  $B_4C$ -YTZP (where YTZP denotes yttriastabilized zirconia polycrystals) mixtures, under an argon atmosphere, generates  $B_4C$ -Zr $B_2$  composites, because of a low-temperature (<1500°C) carbide-oxide reaction. Composites derived from mixtures that include  $\geq 15\%$  YTZP are better sintered than monolithic  $B_4C$  that has been fired under the same conditions. Firing to ~2160°C (1 h dwell) generates specimens with a bulk density of  $\geq 91\%$  of the theoretical density (TD) for cases where the initial mixture includes  $\geq 15\%$  YTZP. Mixtures that include 30% YTZP allow a fired density of  $\geq 97.5\%$  TD to be attained. The behavior of the  $B_4C$ -YTZP system is similar to that of the  $B_4C$ -TiO<sub>2</sub> system. Dense  $B_4C$ -Zr $B_2$  composites attain a hardness (Vickers) of 30-33 GPa.

## I. Introduction

A CCORDING to Krstic and co-workers,<sup>1,2</sup> fully dense  $B_4C-TiB_2$  composites can be obtained via the reactive sintering of mixtures of  $B_4C$ ,  $TiO_2$ , and carbon at temperatures as low as 1900°C (for a minimal oxide content of 10 wt%). The sinterability of  $B_4C-TiO_2$  mixtures was confirmed by Levin *et al*,<sup>3</sup> who fired  $B_4C-TiO_2$  powder compacts (without carbon additions) and obtained  $B_4C-TiB_2$  composites, as did the Krstic groups.<sup>1,2</sup> However, practically useful levels of densification (>90% of the theoretical density (TD)) could be attained only at temperatures of ~2200°C—considerably higher than that indicated by Krstic and co-workers.<sup>1,2</sup> TiO<sub>2</sub> concentrations of ≥35 wt% were required for noticeable densification.

 $B_4C-TiB_2$  (and some other  $B_4C-TrB_2$  mixtures, where Tr is a transition element) composites, of suitable composition, are known to have better strength and toughness than monolithic  $B_4C$ .<sup>1,2,4–7</sup> In regard to  $B_4C-TiB_2$  materials, fracture toughness values as high as 8 MPa·m<sup>1/2</sup> were deemed possible.<sup>2</sup> Improvements regarding the sonic impedance (in comparison with that of pure  $B_4C$ ) also can be expected for some of the  $B_4C-TrB_2$  materials.  $B_4C-TrB_2$  materials seem to be, considering their mechanical properties, practically useful structural ceramics.

Many other transition-element oxides, besides  $TiO_2$ , react with  $B_4C$ . It seems to be of interest to determine whether such reactions  $(B_4C + TrO_x)$  can be used to produce dense  $B_4C/TrB_2$  composites, as well as to compare firing conditions, microstructures, and properties for different  $B_4C-TrO_x$  systems.

In this work, the behavior of  $B_4C-ZrO_2$  mixtures during firing in an argon atmosphere in a temperature range of 1900°–2200°C Adrian Goldstein,\* Ygal Geffen, and Ayala Goldenberg

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was studied. Tetragonal  $ZrO_2$  that had been stabilized to that state via the addition of  $Y_2O_3$  (YTZP) was used.

### **II. Experimental Procedures**

A fine (median particle size of 1.2  $\mu$ m; surface area of ~15 m<sup>2</sup>/g), relatively pure (1.7% oxygen; the total content of iron, silicon, aluminum, and other metals was <0.8%, according to the supplier), near-stoichiometric (B:C ratio of 3.8–3.9) B<sub>4</sub>C powder (H. C. Starck, Goslar, Germany) was used. In addition to the impurities that were listed by the supplier, a tungsten content of 0.6% also was detected. The powder contained agglomerates up to 15  $\mu$ m (10–15 vol%) in size. The second component was a yttria-stabilized polycrystalline tetragonal zirconia (YTZP) powder (Grade HSY-3.0U, Daiichi Kigenso Kagaku Kogyo, Osaka, Japan) that had been stabilized with 5.17% of Y<sub>2</sub>O<sub>3</sub> (~3 mol%), exhibiting a surface area of ~20 m<sup>2</sup>/g. The material is based on crystallites 30–70 nm in size; however, even after hard milling, the smallest independently moving units are first- and second-order, rounded-shape, hard agglomerates 0.1–0.6  $\mu$ m in size.

Green, disk-shaped specimens (25-30 mm in diameter, 4-5 mm thick) were formed via the isostatic pressing (250 MPa) of B<sub>4</sub>C-ZrO<sub>2</sub> mixtures. Their green density (BD<sub>g</sub>) varied over the range of 1.55–1.65 g/cm<sup>3</sup>, as a function of the YTZP content. The most-efficient mixing procedure was determined to be processing in an attrition-type mill; this procedure also ensured that large  $B_4C$ and TZP agglomerates would be dispersed. After drying, the powders were sieved (-20 mesh). Firing was performed in a resistance furnace (Model Astro 1000A, Thermal Technologies, Santa Rosa, CA), in a stagnant argon atmosphere, by placing the specimens in a closed graphite crucible. The heating rate was ~40°C/min up to 1500°C (30 min dwell) and 100°C/min from 1500°C to the sintering temperatures. The temperature range of 1900°-2200°C was examined. Temperatures were measured with a C-type tungsten-coated thermocouple. The firing setup (graphite heating element and crucible, graphite sheets between the specimens) caused the presence of fine carbon particles within the volume of the crucible. As a result, some free carbon may have been adsorbed by the specimens during firing.

Differential thermal analysis (DTA) and thermogravimetry (TG, DTG) were performed (Multisystem 92.14-18, Setaram, Caluire, France).

The bulk density of the fired state  $(BD_f)$  was measured based on the Archimedes technique, and the phase composition was determined from X-ray diffractometry (XRD) (Model PW 1720, Philips Research Laboratories, Eindhoven, The Netherlands). The zirconium concentration in the fired specimens and some green compacts was determined using wet chemistry (gravimetry, precipitation of phosphates). The impurities in the raw materials were determined using X-ray fluorescence. The microstructure—including elemental (Zr, Y) mapping and point chemical analysis—was examined via scanning electron microscopy (SEM). Two systems were used for the SEM analysis (Model SM 3000, JEOL, Tokyo, Japan and Model XL30, Philips (with Link-Isis attachment)). The Vickers hardness ( $H_y$ ) was determined under various loads (from

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Fig. 1. Heat flow and mass variation during the heating of a  $B_4C$ -30-wt%-YTZP mixture to 1500°C at a rate of 5°C/min (HF, differential thermal analysis curve; TG, thermogravimetry curve; and DTG, TG derivative).

200 g to 1 kg) (Model Micromet 2004, Buehler, Lake Bluff, IL). The grain-size distribution was estimated using the procedure that has been described by Mendelson,<sup>8</sup> which was applied to SEM micrographs.

An approximate theoretical density was calculated for the various binary compositions of the  $B_4C-ZrB_2$  system. This approximation was based on the measured zirconium concentrations from which the volumetric percentage of boride was derived.

#### III. Results and Discussion

DTA showed that solid-state reactions between  $B_4C$  and  $ZrO_2$  started at ~1150°C (see Fig. 1). The reaction (after 1 h at 1500°C, all the YTZP had reacted) produced a significant mass loss (~17% for a  $B_4C$ -30%-ZrO<sub>2</sub> mixture that had been heated to 1500°C), which generated ZrB<sub>2</sub> (TD = 6.09 g/cm<sup>3</sup>), as shown in pattern "(b)" in Fig. 2.

Table I shows data regarding the BD<sub>f</sub>, open porosity (OP), and shrinkage ( $\Delta l$ ) after the samples were heated to various temperatures (2060°-2160°C). These data indicate that densification of  $B_4C$ -YTZP powder compacts may proceed further than that of monophase B<sub>4</sub>C, if firing is conducted in a certain temperature range. This range is similar to that of B<sub>4</sub>C-amorphous-carbon powders that can be densified to >90% TD.9 No significant enhancement of the densification is observed at temperatures of <2060°C. The effect is proportional to the YTZP concentration; high YTZP concentrations (~30 wt%) are needed for full densification. Increasing the dwell time from 1 h to 2 h allows the sintering temperatures to be reduced. Densification occurs in the temperature range that, according to Levin et al.,<sup>3</sup> also allows full sintering of the B<sub>4</sub>C-TiO<sub>2</sub> composites. In regard to the differences in the densification of B<sub>4</sub>C-TiB<sub>2</sub> and B<sub>4</sub>C-TiO<sub>2</sub> composites and monolithic B4C, various explanations have been proposed.1-3,10 The formation of boron-rich phases (B:C  $\gg$  4), as a result of the  $B_4C$  + oxide reactions, currently seems to be the most-plausible



**Fig. 2.** Phase composition of green and fired specimens (XRD patterns) at room temperature (pattern "(a)"), 1500°C for 1 h (pattern "(b)"), and 2160°C for 1 h (pattern "(c)"). Legend is as follows: ( $\blacktriangle$ ) B<sub>4</sub>C, ( $\bigoplus$ ) YTZP, and ( $\blacksquare$ ) ZrB<sub>2</sub>.

Table I. Characteristics of B<sub>4</sub>C–ZrB<sub>2</sub> Composites Obtained by Firing at Various Temperatures (2060°–2160°C)

faterial composition (wt% YTZP)	Characteristics		
	BD <sub>f</sub> (%TD)	OP (%)	Δ <i>l</i> (%)
	2060°C for 1 h		
0	77.0	23.0	7.0
7	79.0	21.0	7.5
15	83.0	16.0	9.0
30	86.0	9.0	12.5
	2130°C for 1 h		
0	78.0	22.0	7.5
7	79.0	22.0	7.0
15	86.0	13.0	10.0
30	89.0	7.5	13.0
	2130°C for 2 h		
0	80.0	21.0	8.0
7	83.0	16.0	9.0
15	91.0	1.5	14.0
30	97.0	0.5	17.5
	2160°C for 1 h		
0	83.0	18.5	9.5
7	83.0	15.5	9.0
15	91.0	2.5	13.0
30	97.5	1.0	18.0

explanation regarding the enhancement of matrix sintering for both  $B_4C$ -TiO<sub>2</sub> and  $B_4C$ -YTZP systems.<sup>3</sup>

Submicrometer-sized YTZP particles (the white "haze" on the top surface, shown in Fig. 3(a)), with occasional agglomerates up to 3  $\mu$ m in size, are present in the green specimens. The spatial





**Fig. 3.** SEM micrographs showing the microstructure of fired ( $B_4C-28$ -wt%-Zr $B_2$ ) and green ( $B_4C-30$ -wt%-YTZP) specimens (in backscattered electron imaging (BEI) mode) ((a) surface of as-pressed powder compact (at room temperature) and (b) surface of disk sintered at 2160°C for 1 h).

distribution pattern of the zirconium-containing phases is different in the green and fired states. The fine, quite evenly distributed YTZP particles are transformed to more-localized, larger ZrB<sub>2</sub> grains in the sintered specimens. This phenomenon is illustrated in Figs. 3(a) and (b) and also is confirmed by Zr elemental maps and point analyses that have been conducted on green and sintered specimens. For specimens that have been fired at 2160°C, the ZrB<sub>2</sub> grains and grain aggregates size distribution is 2–15 µm, with an average size ( $\bar{X}$ ) of ~5 µm. Figure 4 shows the morphology and size distribution of the carbide matrix grains, as well as the B<sub>4</sub>C powder particles from which they originated. Most of the carbide grains are 3–10 µm in size ( $\bar{X} \cong 5$  µm). For the material that is based on 30% YTZP, the longest distance between consecutive ZrB<sub>2</sub> grains is 30–40 µm. In materials that initially include ≤15%





**Fig. 4.** SEM micrographs showing the microstructure of the carbide matrix of a  $B_4C-28$ -wt%-Zr $B_2$  specimen ((a) surface formed by indentation (Zr $B_2$  depleted region) and (b)  $B_4C$  (grade HS) powder, as-received).

YTZP, this distance may increase to  $80-100 \ \mu\text{m}$ . In such specimens, the ZrB<sub>2</sub> grains have a tendency to be smaller (on average), their size distribution wider, and their spatial distribution markedly less uniform than that of materials that include  $\geq 25\%$  YTZP. The spatial distribution of yttrium essentially overlaps that of zirconium, which suggests that Y<sup>3+</sup> ions are included in ZrB<sub>2</sub>. This is fortunate, albeit somewhat surprising, considering the high diffusion rates of the Y<sup>3+</sup> ion, at  $\geq 1700^{\circ}$ C, through B<sub>4</sub>C, as well as the fact that compounds such as Y<sub>15</sub>C<sub>19</sub>, YBO<sub>3</sub>, YB<sub>4</sub>, and YB<sub>2</sub>C<sub>2</sub> easily form under the conditions that are existent here during firing.

The hardness of well-sintered (BD<sub>f</sub>  $\ge$  97% TD) specimens (derived from mixtures that include 30% YTZP) was measured. The hardness varied from point to point, in the range of  $H_{\rm V}$  = 30–33 GPa.

#### **IV.** Conclusions

The heating of  $B_4C-YTZP$  mixtures to temperatures of ~2000°C generates  $B_4C-ZrB_2$  composites. Such composites are better densified than monolithic  $B_4C$  in the temperature range of 2060°–2160°C. The improvement in densification is proportional to the YTZP concentration in the green powder compact. When fired to ~2160°C, powder compacts that contain 15 wt% YTZP generate fired specimens with a fired-state bulk density (BD<sub>f</sub>) of  $\geq$ 91% of the theoretical density (TD) (the BD<sub>f</sub> of pure B<sub>4</sub>C is ~83% TD), whereas a BD<sub>f</sub> value of  $\geq$ 97.5% TD is observed for fired specimens that contain 30 wt% YTZP. The behavior of  $B_4C-YTZP$  is similar to that of  $B_4C-TiO_2$  mixtures.

The fully dense  $B_4C-ZrB_2$  composites exhibit a hardness (Vickers) of 30–33 GPa.

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