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# Pressureless sintering of boron carbide

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**Abstract**

The processing of boron carbide by pressureless sintering with and without additives to obtain dense pellets for use as neutron absorber in fast breeder reactors is reported. The effect of particle size and sintering temperature on density and microstructure was studied. Pressureless sintering of boron carbide powder (0.5 μm) at 2375 °C yielded a pellet of 93% $\rho_{th}$. Addition of zirconium dioxide was found to be beneficial in lowering the sintering temperature. A typical sample with 5 wt% zirconia addition sintered at 2275 °C resulted in a density of 93% $\rho_{th}$ and a micro hardness value ($HK_{100}$) of 32 GPa.


*Keywords:* A. Sintering; B. Optical microscopy; C. Hardness; E. Nuclear applications; Boron carbide

## 1. Introduction

Boron carbide is an important non-metallic hard material with high melting point (2450 °C) and hardness. It is generally accepted that in B–C system, one binary phase $B_{13}C_{2\pm x}$ exists with a wide homogeneity range of 8.8–20.0 at.% carbon [1]. Density of boron carbide is 2520 kg/m$^3$, which increases linearly with carbon content within the homogeneity range. Knoop hardness of pressureless sintered boron carbide and hot pressed material are measured as ~25.5 ± 2.4 GPa and ~29.0 ± 1.5 GPa, respectively [2].

Boron carbide is used as neutron absorber owing to its high boron content, chemical stability and refractory character. Neutron absorption property of boron carbide relies on the presence of $B^{10}$ isotope, which undergoes the main capture reaction:

$$_5B^{10} + {}_0n^1 \rightarrow {}_2He^4 + {}_3Li^7 + 2.4\,MeV$$

Absorption cross section of this reaction is 3850 barns for thermal neutrons, which makes it an excellent candidate for thermal reactors. At higher energies the cross section of most other elements becomes very small, whereas that of $B^{10}$ decreases monotonically with energy [3]. Absolute values in the entire energy spectrum are of sufficient magnitude to make it very effective as neutron absorber in the intermediate and fast energy range. Other industrial uses of boron carbide are as abrasive media for lapping and grinding, polishing media for hard materials and as wear-resistant components.

Due to the presence of high fraction of strong covalent bonding, low plasticity and high resistance to grain boundary sliding, densification of stoichiometric boron carbide ($B_4C$) is extremely difficult. Simple shapes of dense boron carbide are industrially prepared by hot pressing under vacuum or inert atmosphere fine (<3 μm) pure powder at a high temperature (2100–2200 °C) and pressures of 30–40 MPa for 15–45 min holding time [4]. In case of boron rich carbides, extensive carbon diffusion takes place from the die material towards the sample. Different metallic foils of Ta, Mo and W and boron nitride barrier can be used for protection. Addition of dopants (Mg, Al, B, Fe, Co, Ni, Cu, $ZrO_2$, $TiO_2$, etc.) can lower the densification temperature to 1750–1900 °C and hinder grain coarsening [1]. A small addition of boron (1–5 wt%) to the starting boron carbide powder gives pellet with the maximum strength in the temperature range of 1900–2000 °C [5]. High density samples were prepared by hot isostatic pressing (HIP) of boron carbide at a lower temperature (1700 °C). However, the problem exists on the choice of canning material.

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Promising results have been obtained by using a special type of boron oxide glass as the canning material [1]. Pressureless sintered material with 1–3 wt% C addition can be fully densified (>99%) by a post HIP treatment at 2000 °C under argon atmosphere of 200 MPa [6]. In pressureless sintering process, dense pellets could be obtained only with a starting material of fine size in the range of $< 3$ μm and a sintering temperature of 2250–2350 °C [1]. Kinetics of recrystallization in sintered and hot pressed boron carbide were investigated by Kuzenkova et al. [7]. They found that recrystallization starts at around 1800 °C and grain grows rapidly above 2200 °C. To increase the volume and grain boundary diffusion and thus to cause densification at lower temperatures different additives are used. Densification at 2150–2250 °C can be achieved by adding different inorganic additives such as Si, Al, Mg, SiC, SiC + Al, $TiB_2$ + C, etc. Recent studies of Levin et al. and Goldstein have shown that the addition of $TiO_2$ [8] and $ZrO_2$ [9] to boron carbide powders improves the density values to 95–97% while sintering at around 2200 °C. The addition of carbon in the form of a novolaque type phenol formaldehyde resin (C is 9 wt%) also yields a dense boron carbide pellet (>95% $\rho_{th}$) [10]. A promising method is the use of two organic precursors, e.g. polycarbosilane with a small amount of phenolic resin [2]. Additives help in the prevention of grain growth and impart better mechanical properties and hardness in the pellets. Recent studies on explosive compaction and subsequent sintering of boron carbide have shown the feasibility of fabricating crack free composites with near theoretical density and high hardness values [11,12].

The present work was aimed at developing a suitable process for the production of dense boron carbide pellets in the density range of 88–93% $\rho_{th}$ for use as neutron shielding in fast breeder reactors. The choice of sintering additives is limited for nuclear application. Though hot pressing method is most suitable for the production of near net shape products, it was not preferred because of its low productivity and high cost. In the above perspective, experimental studies were performed on pressureless sintering of boron carbide. Effects of addition of carbon, titanium boride ($TiB_2$) and zirconium dioxide ($ZrO_2$) on the densification were studied. Pellets were characterized by XRD, optical microscopy, SEM, EPMA and microhardness.

Table 1
Chemical analysis of boron carbide and titanium boride

| Boron carbide | | Titanium boride | |
|---|---|---|---|
| Element | wt% | Element | wt% |
| B | 78.00 | Ti | 67.21 |
| C | 19.05 | B | 30.25 |
| Fe | 1.11 | O | 0.6 |
| Si | 0.45 | C | 0.5 |
| Ni | 0.08 | N | 0.2 |
| Cr | 0.02 | | |
| O | 0.5 | | |

Table 2
Variation of density with temperature

| Serial no. | Particle size (μm) | Temperature (°C) | Density (% $\rho_{th}$) |
|---|---|---|---|
| 1 | 2 | 2225 | 80 |
| 2 | | 2275 | 80 |
| 3 | | 2325 | 85 |
| 4 | | 2375 | 87 |
| 5 | 0.8 | 2300 | 87 |
| 6 | | 2325 | 88 |
| 7 | | 2375 | 93 |
| 8 | 0.5 | 2275 | 81 |
| 9 | | 2300 | 85 |
| 10 | | 2375 | 90 |

## 2. Experimental

### 2.1. Materials

Boron carbide powder used for this study was prepared by carbothermic reduction of boric acid in an Acheson furnace. Chunklets of boron carbide were crushed in a jaw crusher and ground in a hammer mill to obtain particles of less than 45 μm. Fine powders of approximately 1 μm size used in these sintering studies were prepared by micronising these coarse powders in a planetary mill. Impurities picked up during milling were removed by leaching with dilute hydrochloric acid solution. Powders were characterized by chemical analysis and laser particle size analyzer. Fine powders of median diameter of 0.5–2 μm were used in the present investigation. Titanium boride was prepared in the laboratory by the reaction of boron carbide and titanium dioxide in a vacuum induction furnace at a temperature of 1800 °C and a vacuum of $1 \times 10^{-3}$ Pa. Zirconium oxide used was of reactor grade powder obtained from Nuclear Fuel Complex, Hyderabad. Table 1 presents the chemical analysis of boron carbide and titanium boride.

### 2.2. Procedure

In case of carbon addition, the calculated amount of phenol formaldehyde resin (1–3% C) was mixed with boron carbide powder and pelletized. These pellets were slowly heated to a temperature of 1000 °C in argon atmosphere to ensure a fine coating of carbon over boron carbide particles. In other cases, $ZrO_2$ (5 wt%) and $TiB_2$ (5 wt%) powders were thoroughly mixed with boron carbide powder. Powders were then

Table 3
Variation of density with sintering additives

| Serial no. | Sintering additive | Temperature (°C) | Density (% $\rho_{th}$) |
|---|---|---|---|
| 1 | 1 wt% C | 2325 | 91 |
| 2 | 3 wt% C | 2325 | 90 |
| 3 | 5 wt% $TiB_2$ | 2375 | 82 |
| 4 | 5 wt% $ZrO_2$ | 2275 | 93 |

Boron carbide particle size: 0.5 μm.

compacted under a pressure of about 280 MPa to form pellets of 10 mm diameter and 10 mm height with a green density of ~65% $\rho_{th}$. These compacts were sintered in the temperature range of 2225–2375 °C under a dynamic vacuum of $1 \times 10^{-2}$ Pa in a vacuum induction furnace for 60 min. Densities of the pellets were measured using Archimedes principle. Sintered pellets were cut, polished and etched for microscopic observation. A few representative samples were characterized by XRD, EPMA, SEM and micro hardness measurement.

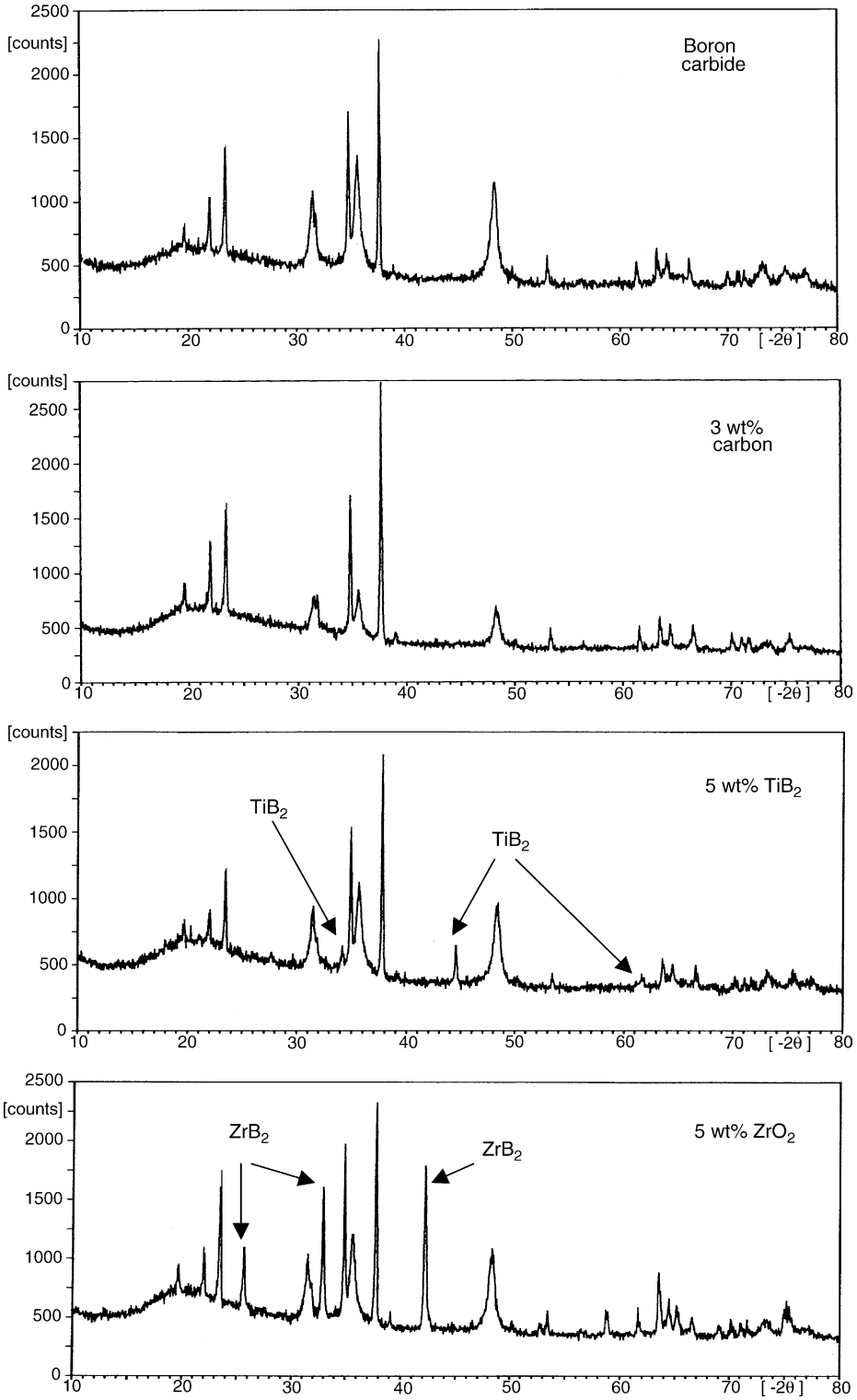


Fig. 1. XRD of the sintered samples.

## 3. Results and discussions

### 3.1. Density

Table 2 presents data on the sintering parameters and densities of pressureless sintering experiments. Pellets sintered in the temperature range of 2225–2275 °C showed densities near 80% $\rho_{th}$. In this temperature range even finer particles of size 0.5 μm also resulted in a density of 81% $\rho_{th}$ only. Densities of the pellets obtained while sintering at temperatures of 2300–2325 °C were in the range of 85–88% $\rho_{th}$. At the sintering temperature of 2375 °C the density of

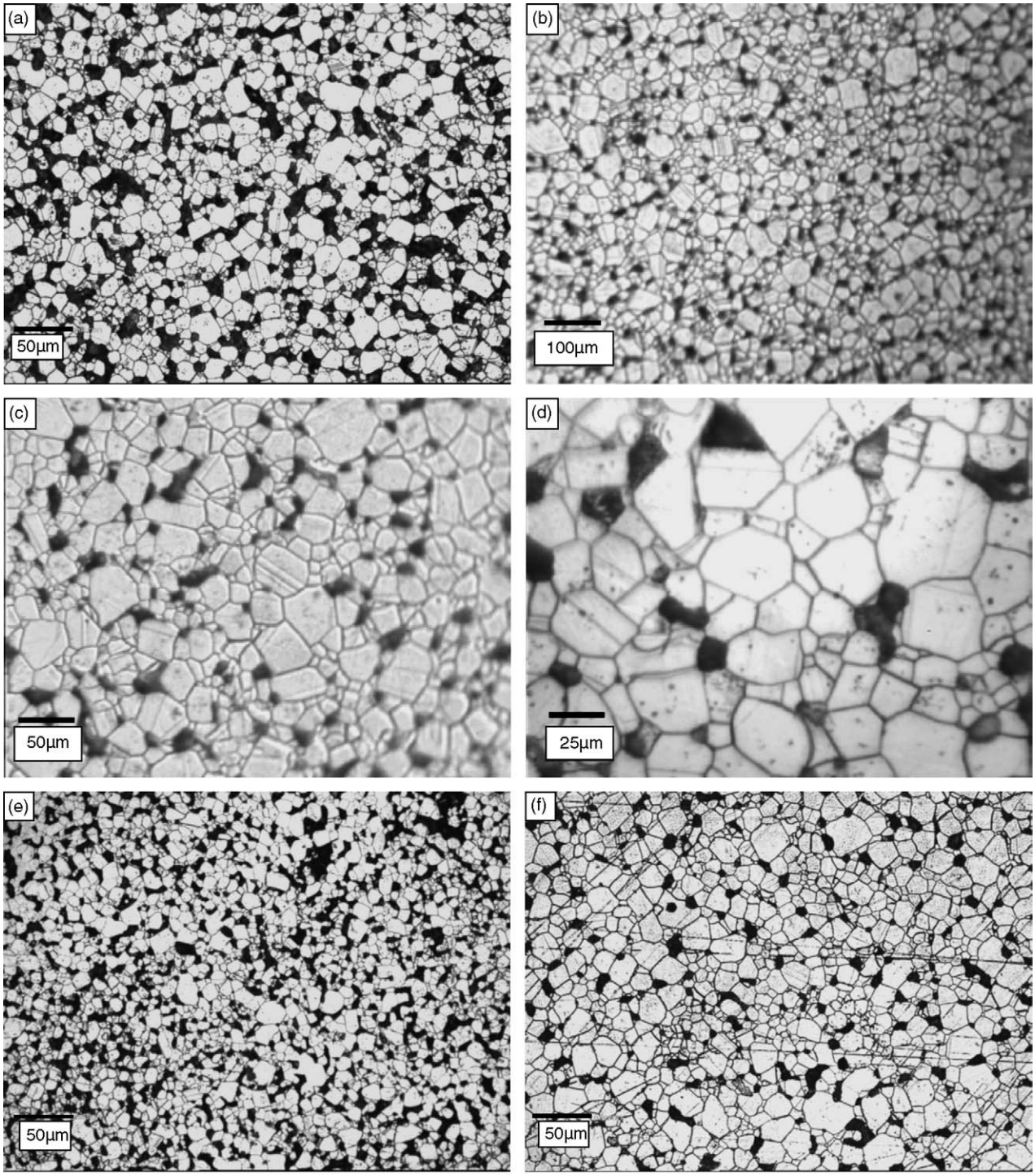


Fig. 2. Microstructure of the sample (a) (0.5 μm) sintered at 2275 °C and (b) (0.8 μm) sintered at 2300 °C. Microstructure of (c) 2b sample at higher magnification and (d) 2c sample at higher magnification. Microstructure of the sample (e) (2 μm) sintered at 2325 °C; (f) (0.8 μm) sintered at 2325 °C; (g) (0.8 μm) sintered at 2375 °C and (h) (0.5 μm) sintered at 2375 °C.

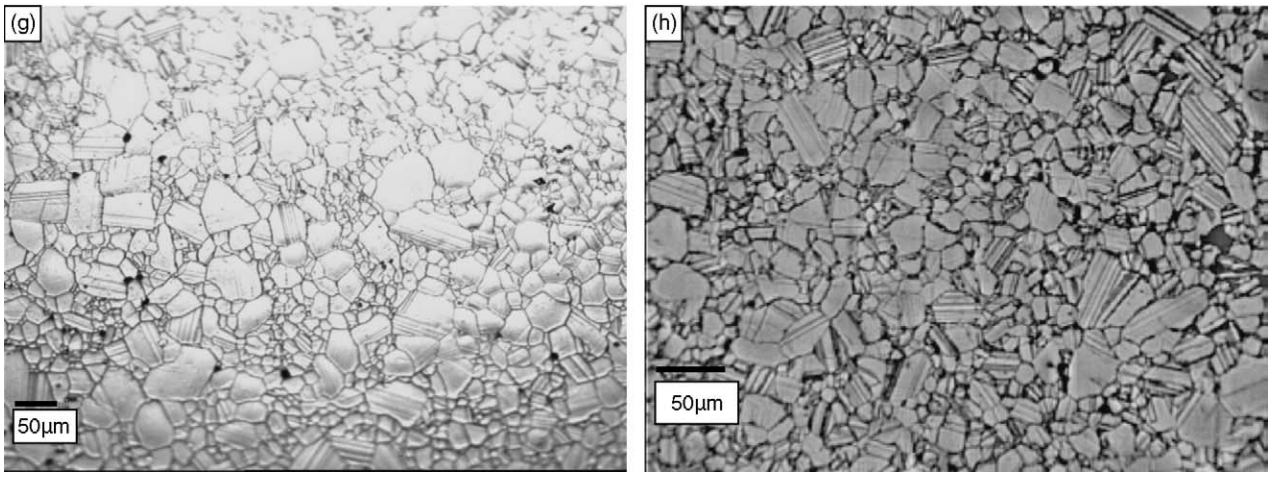


Fig. 2. (*Continued*).

the pellet obtained from 2 μm size particle was 87% $\rho_{th}$ and that of less than 1 μm size particles was above 90% $\rho_{th}$. It can be observed from the above experiments that pellets with densities higher than 90% $\rho_{th}$ could be achieved with a starting material of <1 μm size and a sintering temperature of 2375 °C.

Results on samples sintered with additives are presented in Table 3. Boron carbide sintered at 2325 °C with the addition of 1–3 wt% C showed densities in the range of 90–91% $\rho_{th}$. The addition of 5 wt% $TiB_2$ to boron carbide powder resulted in a lower density of 82% $\rho_{th}$ even at the highest sintering temperature of 2375 °C, whereas addition

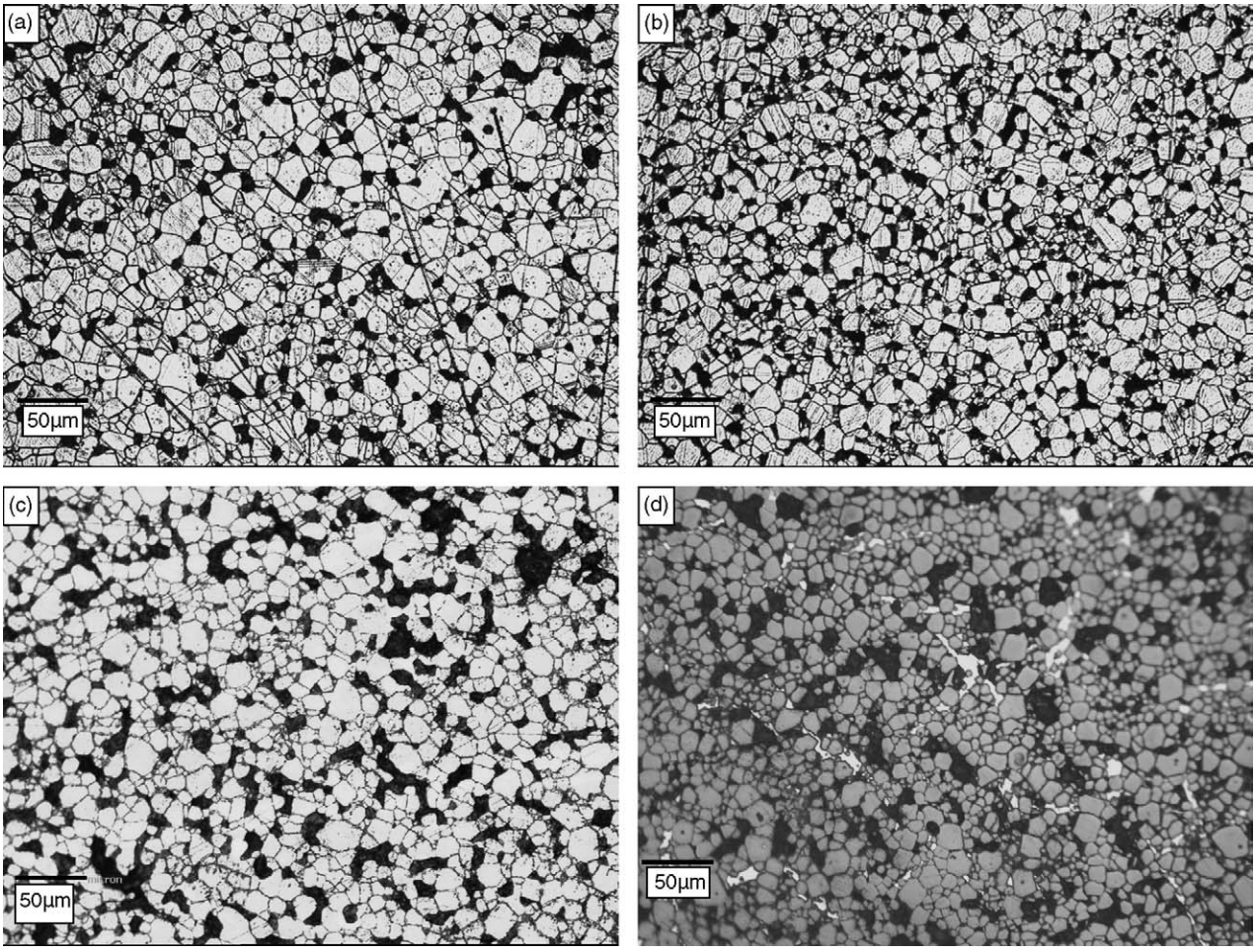


Fig. 3. Microstructure of the sample with (a) 1 wt% carbon addition; (b) 3 wt% carbon addition; (c) 5 wt% titanium boride and (d) 5 wt% zirconium oxide.

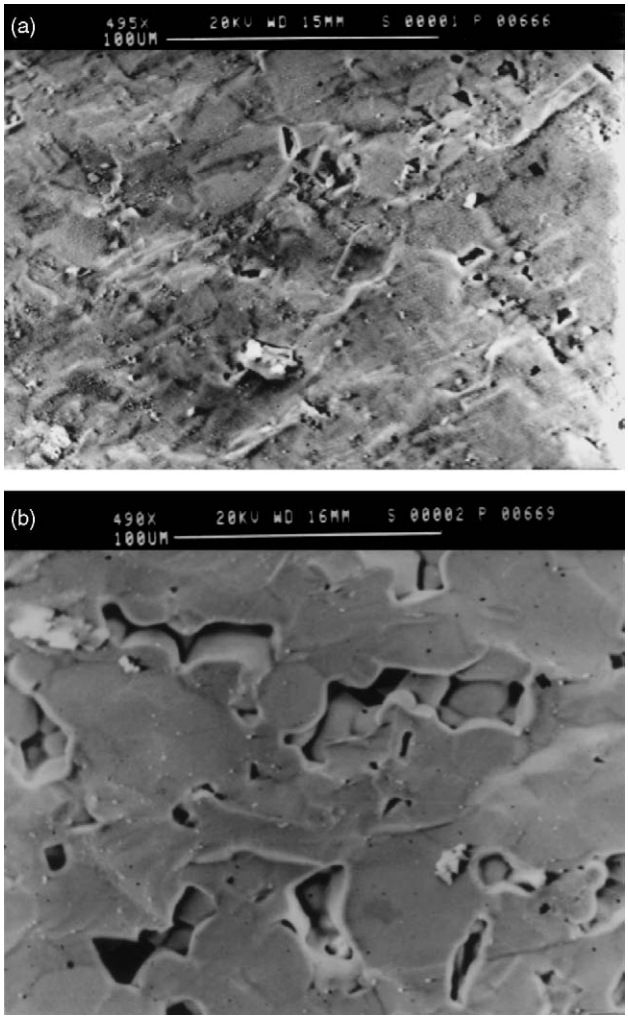


Fig. 4. (a) SEM image of fractured surface of hot pressed boron carbide powder (size: 3 μm, temperature: 1900 °C, pressure: 35 MPa, $\rho_{th}$: 96%). (b) SEM image of fractured surface of pressureless sintered sample containing zirconia (powder size: 0.8 μm, temperature: 2375 °C, $\rho_{th}$: 93%).

of 5 wt% $ZrO_2$ was very effective in achieving a higher density of 93% $\rho_{th}$ even at a relatively lower sintering temperature of 2275 °C. It can be seen from the above results that addition of $ZrO_2$ is beneficial in lowering the sintering temperature of boron carbide.

### 3.2. X-ray diffraction

X-ray diffraction patterns of sintered samples from pure boron carbide and with the additives of C, $TiB_2$ and $ZrO_2$ are presented in Fig. 1. XRD pattern of boron carbide showed the peaks representing $B_4C/B_{13}C_2$ phases. The sample sintered with carbon addition did not show any extra phase other than boron carbide. Pellets sintered with $TiB_2$ did not indicate the formation of any new compound. In the samples sintered with the addition of zirconium oxide ($ZrO_2$) the formation of zirconium boride ($ZrB_2$) was noticed.

### 3.3. Microscopic examination

The microstructures of sintered boron carbide samples are presented in Fig. 2(a–h). Fig. 2a presents the sample sintered at 2275 °C with a particle size of 0.5 μm and a density of 81% $\rho_{th}$. Grains of around 2–20 μm sizes are seen. Pores are mainly interconnected in nature. The presence of a few closed pores is also noticed which indicates the beginning of third stage of sintering. Fig. 2(b–d) present microstructures at different magnification of the sample (0.8 μm) sintered at 2300 °C with 87% $\rho_{th}$. Uniform sized grains with clear grain boundaries are visible. Twining lines are observed inside some of the grains. Closed and uniformly distributed pores (<10 μm) and grains of up to 50 μm are seen. The microstructures of the samples sintered at 2325 °C with particle sizes of 2 and 0.8 μm are given in Fig. 2e and f, respectively. Sample with 2 μm particle size (Fig. 2e) shows the structure quite similar to that of Fig. 2a (2275 °C, 0.5 μm). The sample (0.8 μm) sintered at 2325 °C (Fig. 2f) showed similar features to that sintered at 2300 °C (Fig. 2c). The microstructures of samples sintered at the highest temperature of 2375 °C are presented in Fig. 2(g–h). Important features observed in these cases are presence of well-defined grains, less pore volume, very fine pores and prominent twining lines inside the grains. The appearance of coarse grains indicated the excessive grain growth at this temperature. The size of the larger grains in the case of 0.5 μm sample is 50–60 μm whereas in the case of 0.8 μm is 100–120 μm.

The microstructures of samples sintered with different additives are shown in Fig. 3(a–d). Fig. 3a and b present the sample with 1 and 3 wt% carbon addition, respectively. The addition of carbon helps in refinement of the grains, which can be seen by the comparison of Fig. 3(a and b) with Fig. 2g. This feature is even more prominent in the case of sample sintered with higher carbon content (Fig. 3b). The addition of $TiB_2$ did not help in sintering even at the highest temperature of 2375 °C as can be seen from the Fig. 3c. Microstructure of the sample sintered with 5 wt% $ZrO_2$ reveals the presence of fine precipitates of $ZrB_2$ uniformly distributed throughout the matrix (Fig. 3d).

EPMA analyses showed uniform distribution of boron and carbon within the grains as well as across the grains in all samples. The presence of $ZrB_2$ precipitates is confirmed in samples sintered with the addition of $ZrO_2$ (Fig. 4).

The SEM views of fractured specimens of hot pressed boron carbide (prepared in our laboratory at 1900 °C and 35 MPa with 96% $\rho_{th}$) and pressureless sintered samples are presented in Fig. 4. In both the cases, fracture is transgranular in nature. The hot pressed sample shows presence of very fine pores whereas the pore volume in the sintered sample is more and the size also is large.

### 3.4. Micro hardness

Knoop hardness ($HK_{100}$) of samples with density close to 90% $\rho_{th}$ were measured. Samples sintered without any

additive showed hardness in the range of 24–25 GPa and that of boron carbide densified with the addition of 5 wt% $ZrO_2$ showed a hardness value of 32 GPa.

## 4. Conclusions

Particle size of boron carbide powder and the sintering temperature are two most important parameters for densification by pressureless sintering. Density obtained from sintering studies at temperatures below 2300 °C was observed to be less than 85% $\rho_{th}$ irrespective of the particle size in the range of 0.5–2.0 μm. At the highest sintering temperature of 2375 °C a fine particle size of 0.5/0.8 μm was helpful in getting a density of above 90% $\rho_{th}$. The addition of carbon helped in achieving densities of 90–91% $\rho_{th}$ at a lower sintering temperature of 2325 °C as well as in grain refinement. $TiB_2$ addition was not found to be helpful in sintering. $ZrO_2$ as sintering additive was found to be very effective in reducing the sintering temperature. A dense pellet of 93% $\rho_{th}$ could be achieved by sintering with 5 wt% $ZrO_2$ at a comparatively lower temperature 2275 °C. In all the cases it was observed that distribution of boron and carbon was uniform throughout the matrix. Knoop hardness ($HK_{100}$) of sintered boron carbide was measured as 24–25 GPa and that of sintered with $ZrO_2$ as 32 GPa.

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