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Effect of carbon and titanium carbide on sintering behaviour of zirconium diboride

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Abstract

Systematic sintering studies on the ZrB_2 powder were carried out with the addition of carbon (C) in the range of $0 < x < 10$ (x = wt.%) and (titanium carbide) TiC in the range of $0 < y < 30$ (y = wt.%). Zirconium diboride powder made by different routes showed similar sintering behaviour and amongst all the powders, the SHS made powder exhibited most homogeneous morphology. The addition of C facilitate densification in the range of $0 < x < 4$ and hinders densification for $4 < x < 10$, whereas, the addition of TiC above 5 wt.% was found to be detrimental for the sintering of ZrB_2. The addition of C also found to inhibit the grain size and fine grained ZrB_2–C composite could be obtained with high densification. The increased densification with the C addition was due to removal of oxygen impurities on the ZrB_2 powder surfaces that prevented the commonly observed exaggerated grain growth through evaporation condensation of oxide phases during sintering of boride ceramics. At higher percentages of C addition, the densification rates decreased due to increased volume fraction of second phase that acted as diffusion barrier.

Keywords: Borides; Composites; SHS; Sintering; Microstructure

1. Introduction

The diborides, particularly the ZrB_2 and TiB_2 are important high temperature ceramics. They have similar crystal structures and possess excellent high temperature properties such as high hardness, high elastic modulus, excellent oxidation resistance and chemically stability in many corrosive environments [1,2]. Zirconium diboride does not have many intermediate phases compared to TiB_2, which makes ZrB_2 a favourable candidate over TiB_2. It is a potential material for use at elevated temperatures with good abrasion, wear and corrosion resistances both in terms of bulk as well as protective coatings. For bulk applications, loosely packed compacts need to be sintered and fabrication of monolithic zirconium diboride by sintering technique is difficult due to its high melting temperature and covalent bonding. Most often ZrB_2 is sintered at 2000–2200 °C [3–5] and the pressureless sintering studies are very limited. One of the crucial problems faced during sintering of borides is the exaggerated grain growth during sintering [6,7], which hinders the densification process. Following the initial stage of rapid shrinkage (presumably by grain-boundary diffusion process), excessive coarsening is induced by the partial predominance of evaporation–condensation mechanism at the densification temperatures and results in a rapid diminution of the driving force for sintering. The presence of thin oxygen rich layer on the surface of boride powders is reported to be detrimental for densification of borides [8,9].

Improvement of physical and chemical behaviour of the ZrB_2 ceramics is possible by incorporating other high-temperature ceramic materials into the ZrB_2 matrix. So far several additives have been used to make the diboride-based composites and it has also been aimed to counter the grain growth for enhancing the sintering process and yield good sintered bodies. Most of the studies on sintering additives such as NiB, TiC, TaC, CrB_2 Ni, Fe, Co, Mo, B_4C, etc. are being reported on the TiB_2 system [10–14] and a few are reported on the ZrB_2 system, which is expected to behave similar to the TiB_2 system. The addition of NbB_2 and CrB_2 was found to prevent the grain growth during hot pressing of TiB_2 and the addition of Ni and TaC increased the pressureless shrinkages of TiB_2 via liquid phase and chemical gradient effects [15,16]. A very

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small percentage of Fe (0.5 wt.%) initially enhanced the densification rates but at higher percentages poor densification was resulted with occurrence of large grain growth. The B_4C addition along with 0.5 wt.% of Fe had shown remarkable suppression of grain growth but when added with higher percentages (more than 0.5 wt.%) no significant effect was observed and B_4C was trapped inside of large titanium diboride grains [17]. The addition of TiN was also shown to improve the properties [18]. The addition of silicon carbide to TiB_2 showed remarkable improvement in densification behaviour of TiB_2 by eliminating the oxide layer that existed on the surface of the powder [19]. The addition of Si_3N_4 to titanium diboride resulted in better densification but the glassy phases of Si–Ti–O–N at grain-boundaries degraded the mechanical properties [20].

So far, a few studies reported the addition of NiB, Cu, Mo, etc. with ZrB_2 [21]. The addition of 15 wt.% Mo to ZrB_2 found to be the optimum composition for obtaining the highest density. It was also observed that the addition of Mo formed the MoB and ZrC phases during processing. The addition of Cu resulted liquid phase sintering and the addition of metal up-to a few percentage only help in sintering. It also limited the strength, hardness and other properties of the composites. Besides the sintering aids, the powder preparation techniques also have significant effect on the final properties of the product. Compared to the conventional carbothermic process other non-equilibrium processes such as plasma arc technique had shown better properties due to high purity of the product and high surface area of the synthesised powder [5]. The SHS processing is an attractive non-equilibrium processing technique, which is fast & energy efficient [22,23]. The SHS produced powder also had high defect concentration in the powders, which could be helpful in enhanced sintering [24]. In the present paper, a comparative study on the effect of C and TiC on the sintering behaviour of ZrB_2 powder prepared by different techniques has been reported.

2. Experimental

Zirconium diboride powders used in the present investigation were made by SHS and carbothermic routes. The details of the synthesis procedures are briefly described in the following sections. The sintering behaviour of the synthesised powders was also compared with the commercially available zirconium diboride powder (Aldrich, USA).

2.1. Preparation of ZrB_2 and TiC powder by SHS process

Zirconium diboride (ZrB_2) and TiC powders were synthesised by SHS process (arc ignition technique) using zirconia, boric acid and magnesium as the starting powder. The details of the process are described elsewhere [25]. Titanium carbide was also prepared using the mixture of Ti and amorphous C powder. The details of the process for the TiC powder preparation using SHS technique is also been reported [26]. The SHS reactions for the synthesis of zirconium diboride and TiC are given below.

$$ZrO_2 + 5Mg + 2H_3BO_3 = ZrB_2 + 3H_2O + 5MgO$$

$$Ti + C = TiC$$

The by-product of SHS reaction MgO was leached by dissolving in HCl and the product (ZrB_2) was filtered and washed with distilled water and alcohol. The powder was then dried in an oven at 150 °C.

2.2. Preparation of ZrB_2 powder by carbothermic process

In the carbothermic process, zirconium diboride powder was prepared using zirconium dioxide, boron oxide and carbon by the following reaction:

$$ZrO_2 + B_2O_3 + 5C = ZrB_2 + 5CO$$

The starting powders of zirconia, boron oxide and carbon were taken in stoichiometric quantities and then mixed in a planetary ball mill (Retsch, PM400 Germany) for 30 min at 250 rpm rotation. The mixture was subsequently heated at 1800 °C for 30 min in a resistive heating graphite furnace (Thermal Technology Inc., USA) and then furnace cooled down to room temperature.

2.3. Powder compaction and sintering study

Zirconium diboride powder synthesized by SHS and carbothermic routes and the commercial ZrB_2 powder were mixed with 2, 3, 4, 5 and 10 wt.% of C in five different batches. Similarly, 5, 10, 20 and 30 wt.% of TiC (made by the SHS technique) were also added with the ZrB_2 powders. The C and TiC added ZrB_2 powder was milled in a planetary ball mill to increase homogeneity of the powder mixture. The mixed composite powder was pressed into the form of 3 mm thick pellets having a diameter of 15 mm. All these pellets were sintered at 1800 °C for 30 min in a graphite furnace under flowing argon gas followed by slow cooling down to 1300 °C and then furnace cooled down to room temperature. The microstructure and composition analyses were carried out using SEM (JEOL-JSM 800, Japan). The phase analyses were carried out by X-ray diffraction pattern using Simens powder diffractometer (Germany). The densities of the samples were measured by liquid immersion technique in water medium using Archmedies principle with an accuracy of ±1%.

3. Results and discussion

3.1. Characterisation of the starting powders

The X-ray diffraction (XRD) analyses of the synthesised ZrB_2 powders (by SHS and carbothermic routes) showed the peaks of ZrB_2 as the main phase in the patterns. Minor peaks due to ZrO_2 were also observed in the patterns. The SHS made ZrB_2 and TiC powder was found to be sub-micrometer in size, whereas, the carbothermically prepared powder were found to be micrometer in size. The commercial powder was found to be single-phase materials (without any zirconia peaks) and its particle sizes were also in the micrometer range. The SHS produced TiC powder was found to be a single-phase material and they were agglomerated with sizes $>10\ \mu m$. The scanning or transmission electron micrographs of the ZrB_2 powder prepared by different processes and the SHS made TiC powder are shown in Fig. 1.

3.2. Effect of C addition to zirconium diboride

The XRD patterns of sintered ZrB_2 pellets (made from the SHS prepared powder with various C contents, 2–10 wt.%) showed the presence of ZrB_2 phase with very feeble peaks of $ZrC_{0.7}$ phase (Fig. 2). The densification behaviour of the ZrB_2–C pellets sintered at various temperatures is shown in Fig. 3a, which showed that the increase of measured densities from 87 to 94% with the increase of C content from 0 to 4 wt.% and further increase of C to 10 wt.% led to the decrease of densification. The observed increase in the density for smaller percentages of the carbon addition was due to the fact of that the borides

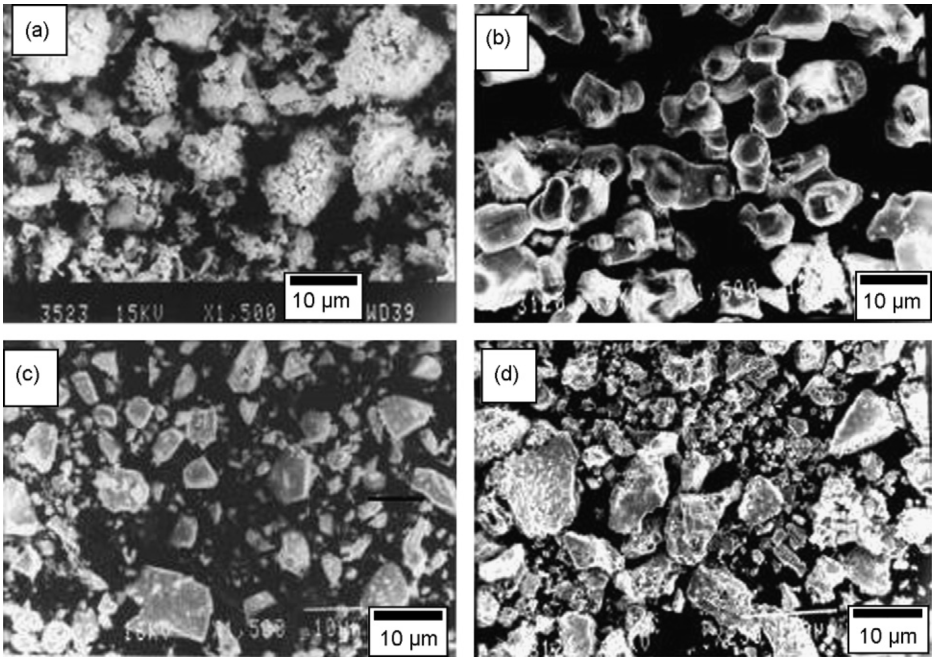

Fig. 1. Scanning electron micrographs of the starting powder (a) ZrB_2 powder by SHS route, (b) ZrB_2 powder by carbothermic, (c) commercial ZrB_2 powder and (d) TiC powder by SHS route.

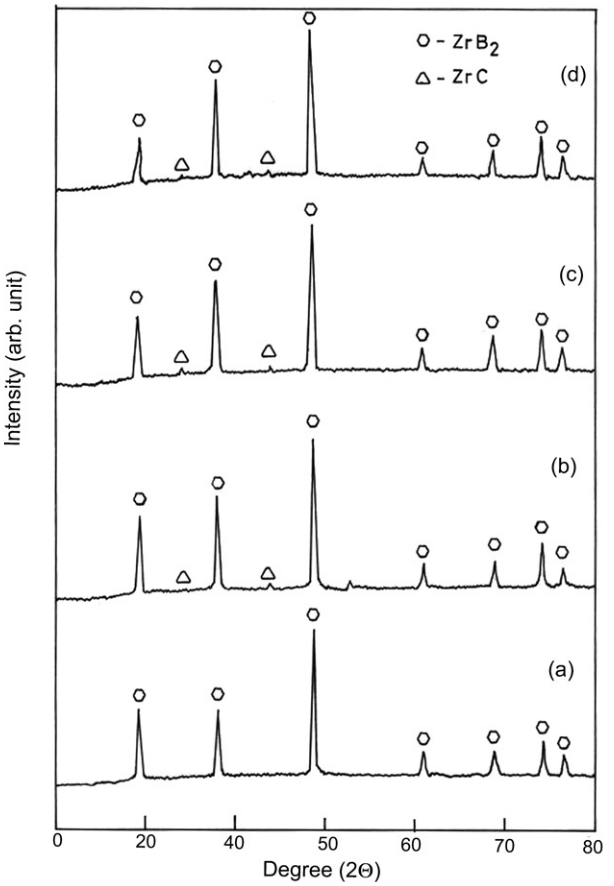

Fig. 2. XRD patterns of ZrB_2 pellets (SHS) sintered at 1800 °C for 30 min with different C contents: (a) 0, (b) 2, (c) 5 and (d) 10 wt.%.

always have oxygen at the surface, which was reduced by added carbon while sintering at high temperature. Hence the surface became more active and helped in sintering. From the densification curve (Fig. 3a) it was apparent that beyond a certain concentration, the excess free carbon was not taking part in the sintering process, rather it hindered the mass transport processes. Hence with higher percentages of C contents, the sintered pellets were less dense and remained porous. Scanning electron microscopy on the fractured surfaces of the sintered ZrB_2 pellets with 0–5 wt.% of C addition showed insignificant grain growth during sintering (Fig. 4). From the microstructures compared to that of the samples sintered without C addition, the grain growth could be inhibited to a good extent. The microstructure of

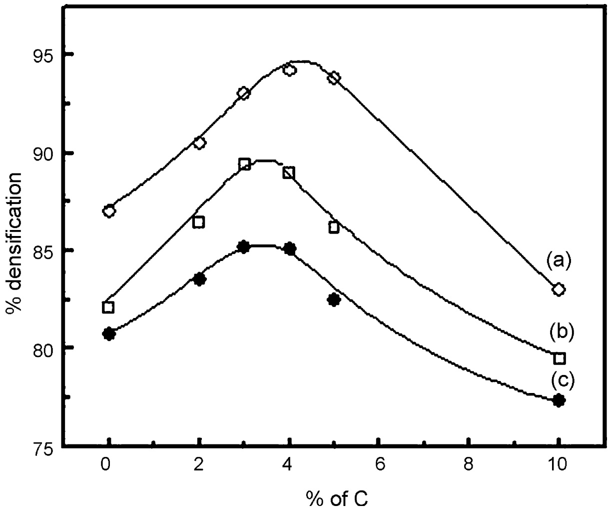

Fig. 3. (a–c) Densification behaviour of the SHS produced ZrB_2 powder with different C contents.

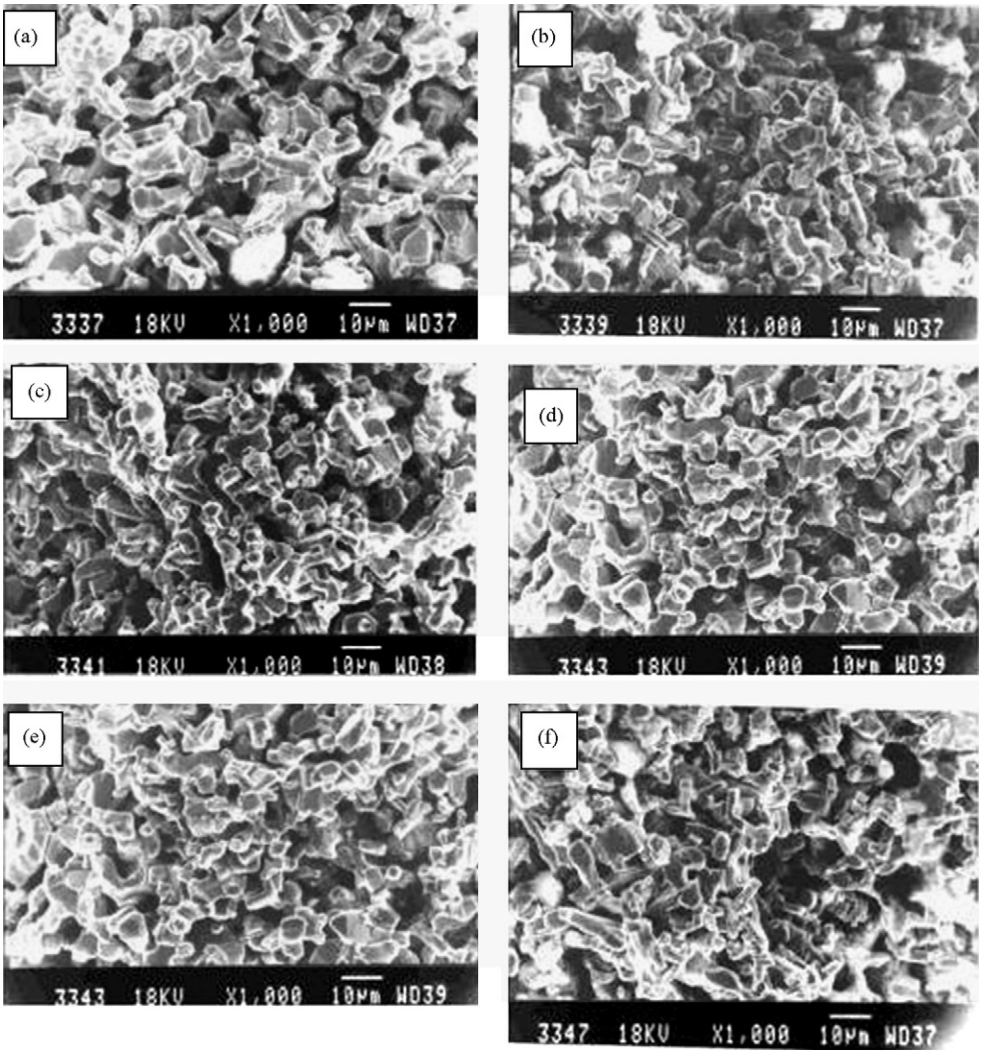

Fig. 4. SEM micrographs of the fractured surfaces of ZrB_2 pellets (SHS) sintered at 1800 °C for 30 min with different C concentrations: (a) 0, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 10 wt.%.

the sintered pellet was also found to be homogeneous throughout the samples and the porosity was much less compared to the samples where no C was added. The SEM/EDX analyses showed the presence of Zr only in all the sintered grains (the present detector cannot detect B & C peaks). From the XRD analyses, the sintered samples were found to be a single-phase material and therefore the grains showing Zr peaks in the EDX spectra were from the ZrB_2 grains only. The sintered sample surface added with carbon was found to be electrically conducting with a conductivity in the range of 300–400 μΩ cm), whereas the top upper layer surface was non-conducting when carbon was not added and the inside bulk material was conducting. The formation of zirconia layer on the surface of the pellets sintered without C addition is shown in Fig. 5. This oxide scaling on the surface of sintered pellets indicated the movement of oxygen towards the surface of the pellets during sintering when no carbon was added. In the presence of C, the oxygen reacted with C and no oxide formation on the surface was observed. Therefore, the C addition was found be beneficial in purifying the material, which needed optimisation of the carbon content.

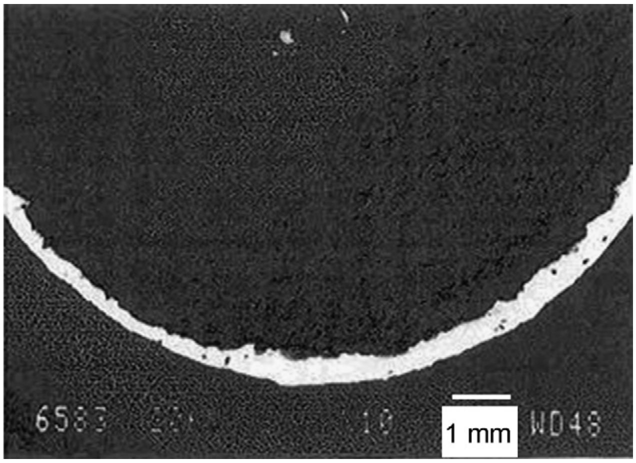

Fig. 5. SEM micrographs of ZrB_2 pellets (SHS) sintered without C addition at 1800 °C for 30 min showing the oxide scale formation.

Similar densification and phase formation behaviour was observed in the case of carbon added ZrB_2 (carbothermic) powder when sintered at 1800 °C for 30 min. The pellets sintered with 2 wt.% of C showed the appearance of ZrB_2, ZrO_2 along with very feeble peak of ZrC and further increase of C showed only the presence of ZrB_2 and ZrC phases in the XRD patterns. The density was found to increase initially (∼89% for C = 4 wt.%) and later decreased for further increase of carbon addition (Fig. 3b). Scanning electron micrographs of the fractured surfaces of the ZrB_2 samples sintered at 1800 °C with 2, 5, 10 wt.% of carbon additions showed controlled grain growth and homogeneous morphology throughout the sintered samples (Fig. 6). The samples, which had 10 wt.% of C showed large micro-pores with exaggerated grain growth in some localised places, which was the reason for observed decrease of density. The observed increase in grain size at higher percentages of the carbon was due to inhomogenieties in the mixture, which on sintering facilitated the grain growth where no carbon was present. In that case, the boride–boride grains grow as it happens in normal sintering process. The increased porosity in the higher carbon content in the sample was resulted in abnormal grain growth at localised places.

The commercial ZrB_2 powder having only ZrB_2 phase also showed the presence of feeble ZrC peaks in the XRD patterns.

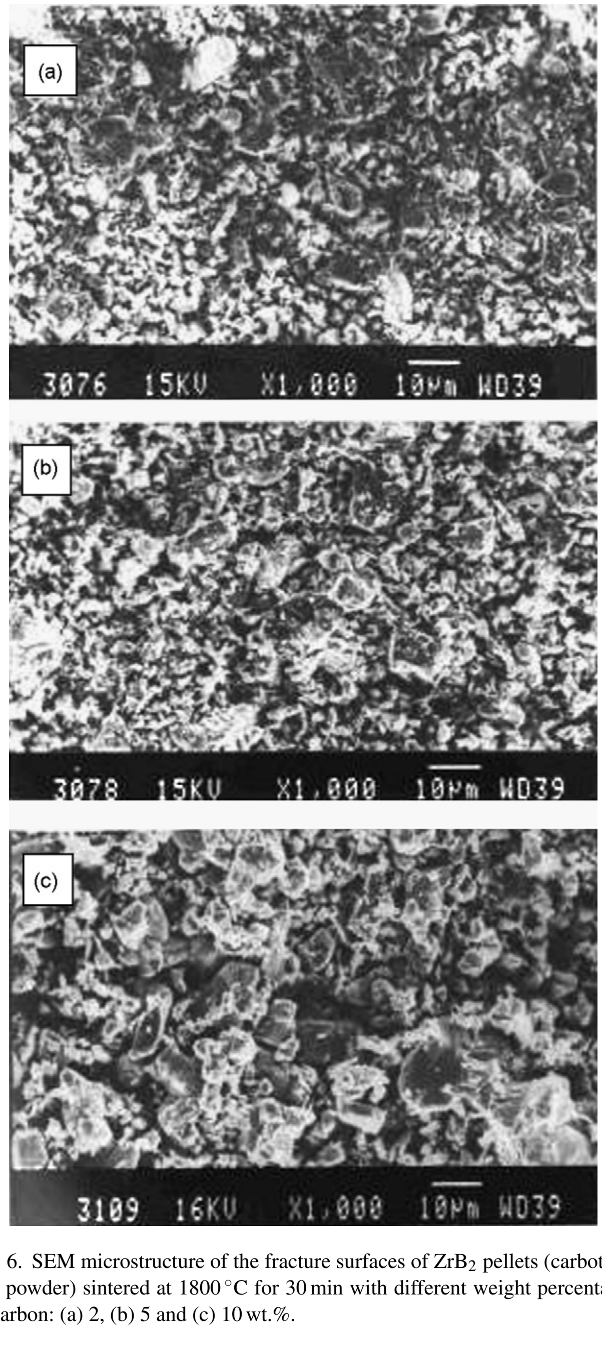

Fig. 6. SEM microstructure of the fracture surfaces of ZrB_2 pellets (carbothermic powder) sintered at 1800 °C for 30 min with different weight percentages of carbon: (a) 2, (b) 5 and (c) 10 wt.%.

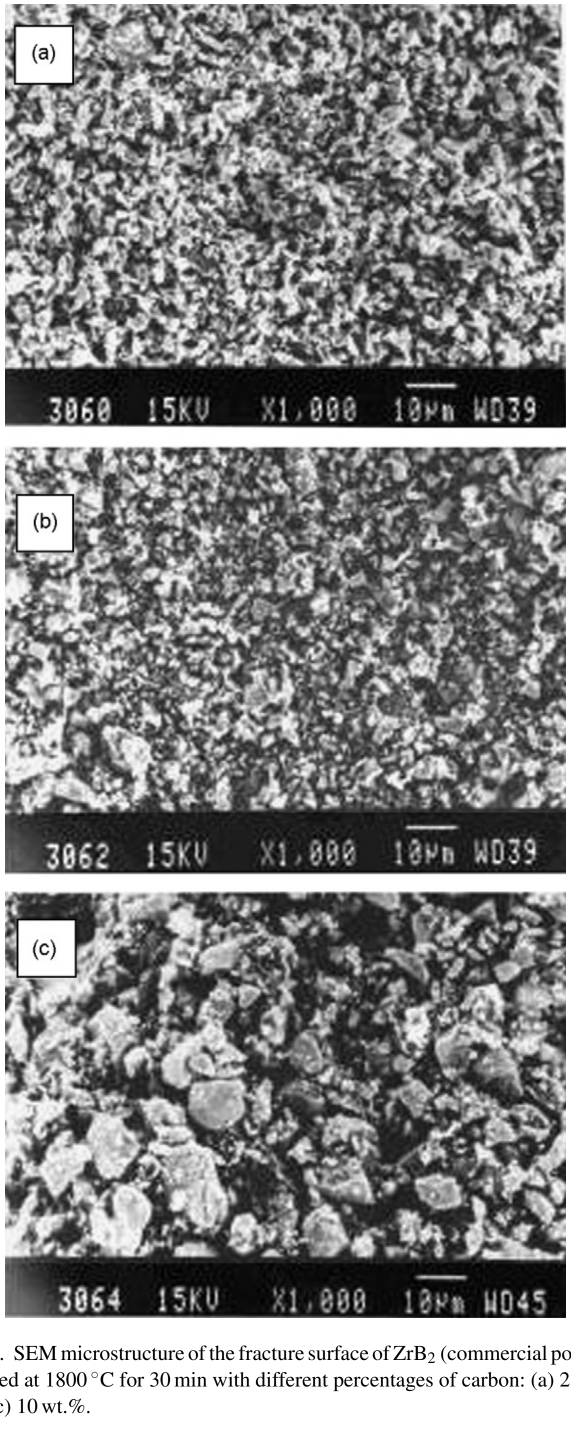

Fig. 7. SEM microstructure of the fracture surface of ZrB_2 (commercial powder) sintered at 1800 °C for 30 min with different percentages of carbon: (a) 2, (b) 5 and (c) 10 wt.%.

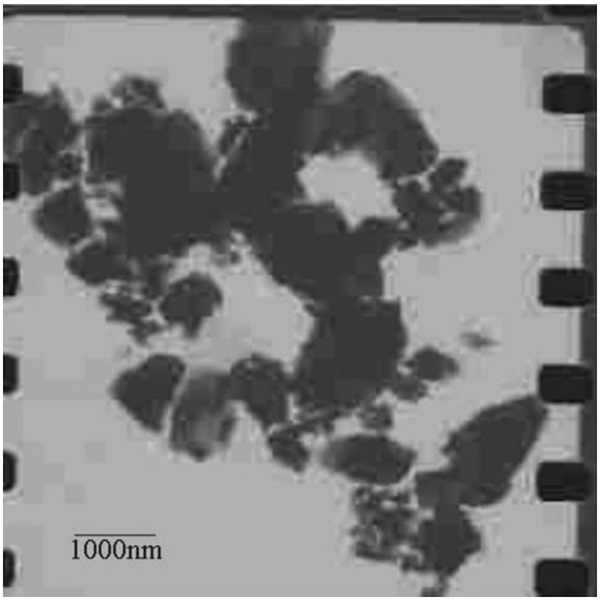

Fig. 8. TEM micrographs of ZrB_2 powder showing agglomeration.

Similar trend of densification was also observed with the addition of C, where densification increased to 85% for 3 wt.% of C addition and further increase of C content led to decrease in densification (Fig. 3c). The commercial powder revealed two types of particles during SEM observation, one was very fine and other was large in size. Whereas, the microstructure of the sintered samples showed a contrasting features of homogeneous morphology with fine grains through out the samples (Fig. 7). With the addition of C up to only 2 wt.%, uniform microstructure is resulted and further addition of C to 5 wt.% did not reveal any significant changes in the microstructure. The samples added with 10 wt.% of C expectedly showed significant grain growth during sintering. The porosity of the samples also increased with the grain growth. The abnormal grain growth and decreased densification is possibly due to same reason as in the case of sintering of carbothermic or SHS made ZrB_2 powder (Fig. 7c).

The apparent reduction in grain size is due to deagglomeration of the powder during high temperature sintering. It is well known that agglomerated particles undergo coarsening before the first stage of sintering and one of the concerns in ceramic processing technique is the control of agglomeration, since an agglomerated powder is of little benefit during densification as coarsening prevails over sintering. From the transmission electron microscopy studies it was apparent that the starting powders were agglomerated and it contained large numbers of crystallites (Fig. 8). It is also known that Vander walls or hydrogen type of bonding are the cause of weak-agglomeration in ceramics. In this case, these bonds are due to presence of oxide layer on the powder surface and it is irrespective of the powder preparation techniques the oxide layer is present on the powder surface. During sintering, C reacted with the oxide layer and removed the agglomeration. Therefore, the apparent decrease in grain size is due to deagglomeration.

The effect of carbon is quite clear for the fine SHS made ZrB_2 powder (<100 nm prepared by milling in vibratory cup mill using WC grinding media), which was sintered at 1800 °C for 30 min. The TEM image of the milled powder is shown in Fig. 9a. The sintered pellets without any carbon addition achieved a densification of 90% of the theoretical density, whereas the 5 wt.% carbon added samples achieved densification >94%. The samples sintered without any carbon addition showed large

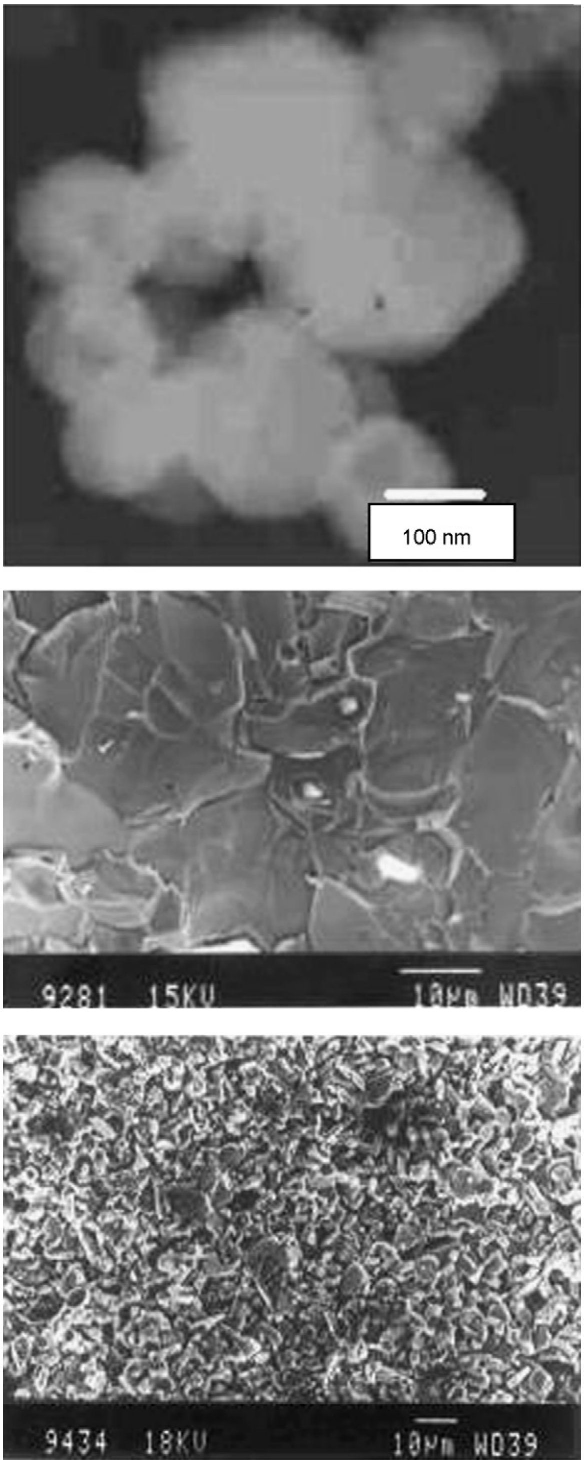

Fig. 9. (a) TEM micrograph of nano-crystalline ZrB_2 powder. (b) SEM microstructure of the ZrB_2 pellet sintered without carbon at 1800 °C for 30 min and (c) SEM microstructures of the ZrB_2 pellet sintered with 5 wt.% carbon at 1800 °C for 30 min.

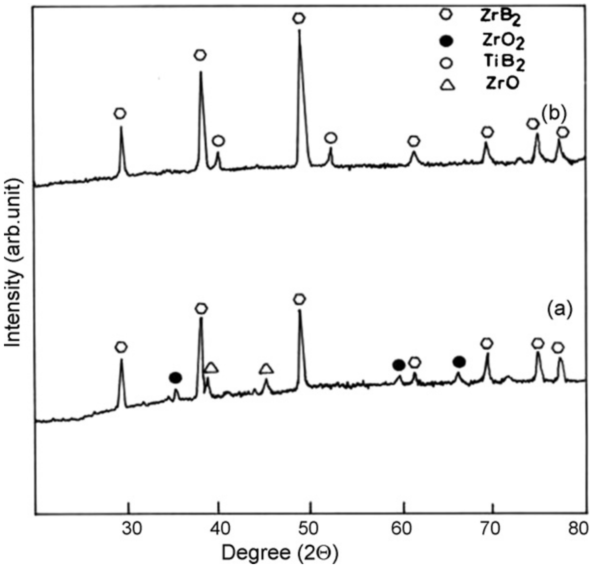

Fig. 10. XRD patterns of ZrB_2 pellets made from SHS powder and sintered at 1800 °C for 30 min with: (a) 0 and (b) 20 wt.% of TiC.

coarsening of grains (Fig. 9b) and the 5 wt.% carbon added samples had fine grain structures throughout the pellets after sintering (Fig. 9c). This clearly indicated the role of C on grain growth inhibition of zirconium diboride ceramics.

3.3. Effect of TiC addition to zirconium diboride

The XRD pattern for the samples added with 5 wt.% of TiC (SHS made) did not show any additional peaks, but the 10 wt.% of TiC added ZrB_2 sample showed the low intensity additional peaks of TiB_2. No TiC peak could be observed in the XRD pattern. This is due to reaction between ZrB_2 and TiC during sintering at 1800 °C by the following reaction:

$$ZrB_2 + TiC \rightarrow TiB_2 + ZrC$$

The ZrC peaks could not clearly be observed in the XRD patterns due to low percentage of it in the sample. However, careful observation of the pattern could reveal the small peak due to ZrC phase. The XRD patterns of sintered samples with different percentages of TiC are shown in Fig. 10. During sin-

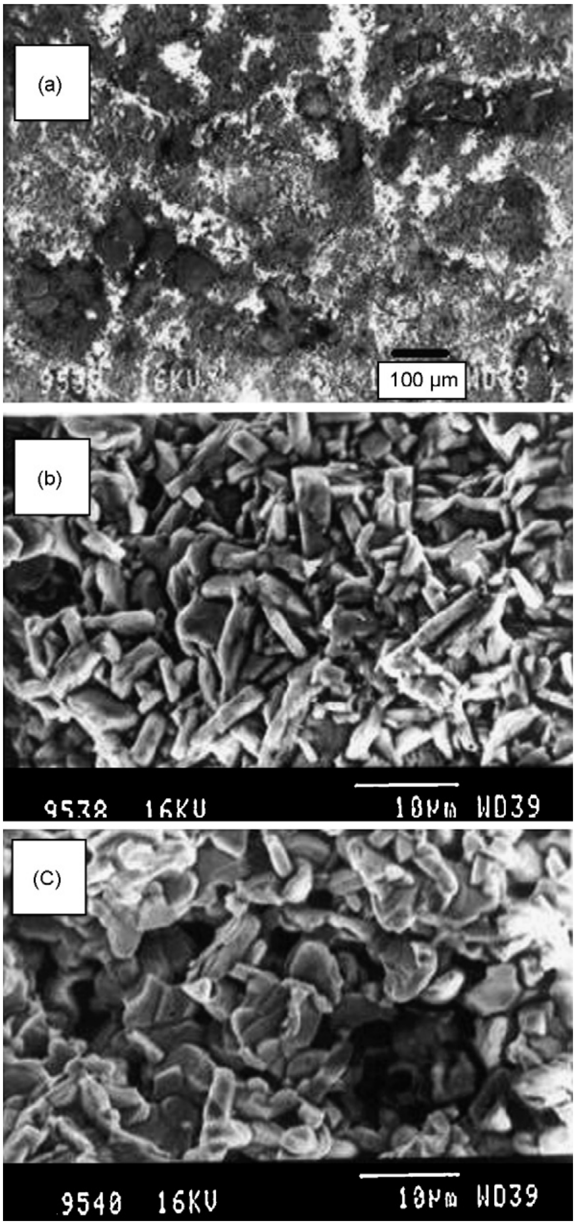

Fig. 12. SEM microstructures of ZrB_2 pellets sintered sample with 10 wt.% TiC: (a) showing two types of regions, (b) Ti rich area showing elongation of grains and (c) Zr rich area.

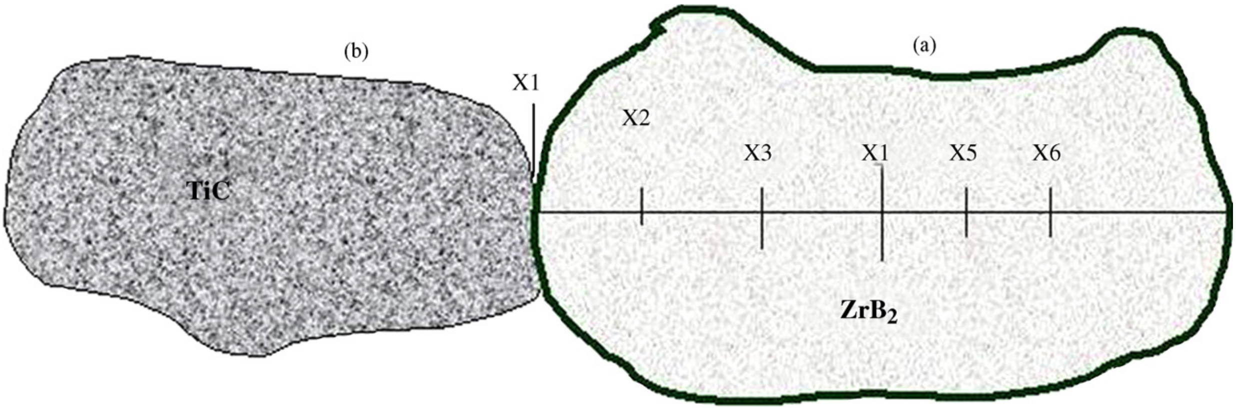

Fig. 11. Schematic of the EDX point analyses: (a) ZrB_2 grains and (b) Ti-containing grains.

Table 1
Density ZrB_2–TiC (By SHS) composites sintered at 1800 °C

Sample	Theoretical density	Measured density	%Densification
ZrB_2 (initial powder)	6.0	5.22	87
ZrB_2 (5% TiC)	5.656	5.33	94.2
ZrB_2 (10% TiC)	5.349	3.57 (4.6)	86

Table 3
Bulk EDX analyses of Zr and Ti rich area in ZrB_2 sample having 10% TiC

Element	Zr rich area	Tr rich area
Ti (wt.%)	4.31	69.03
Zr (wt.%)	95.69	30.17

tering some of the TiC might be going into solution with ZrB_2 forming a complex boride and the rest is reacting and formed the TiB_2 phase. The density was found to increase to 94% of the theoretical density compared to 87% for the sample sintered without TiC (Table 1). The microstructures of the sintered samples are shown in Fig. 11, which showed less grain growth in the TiC added samples. Low magnification studies revealed that the sample added with 10 wt.% of TiC had two types of areas in the samples, one having larger percentages of Ti and other with Zr. The EDX analysis at the grain boundaries and inside the grain for 5 wt.% TiC added sample showed the diffusion of TiC/Ti into ZrB_2 grains, but no diffusion of Zr was observed in Ti-containing grains. For understanding the interdiffusion of Zr and Ti, systematic EDX point analyses, with probe size of the order of 20 nm, at different points of the grain from grain boundary to middle of the grain and beyond schematically shown in Fig. 12 and the elemental analyses are presented in Table 2. From which it is clear that Ti/TiC had diffused in the ZrB_2 grains making it as complex boride and had graded diffusion from grain-boundary. The bulk EDX analyses of the Ti and Zr rich areas are given in Table 3. The Ti rich areas showed some elongation of grains whereas Zr rich areas showed controlled grain growth (Fig. 11). The densification of 10 wt.% of TiC added samples decreased to 85%. This observed decrease in densification was due to the observed segregation and also due to formation of TiB_2, which was not considered during density calculation. Besides these, the other causes may be the presence of second phases, which hinders the sintering of the composite.

Similar densification and phase formation behaviour was observed for the carbothermic and commercial powder. The scanning electron microscopy studies reveal that the samples became more porous and fragile as the TiC content increased above 5 wt.% and it was difficult to measure densities of the

Table 2
EDX analyses of ZrB_2 grain and grain boundary for ZrB_2 sintered sample having 5% TiC

Element	X1 (grain boundary)	X2	X3	X4 (middle)	X5	X6
Ti (wt.%)	5.39	5.01	4.18	4.01	4.04	4.99
Zr	94.61	94.99	95.82	95.99	95.96	95.01

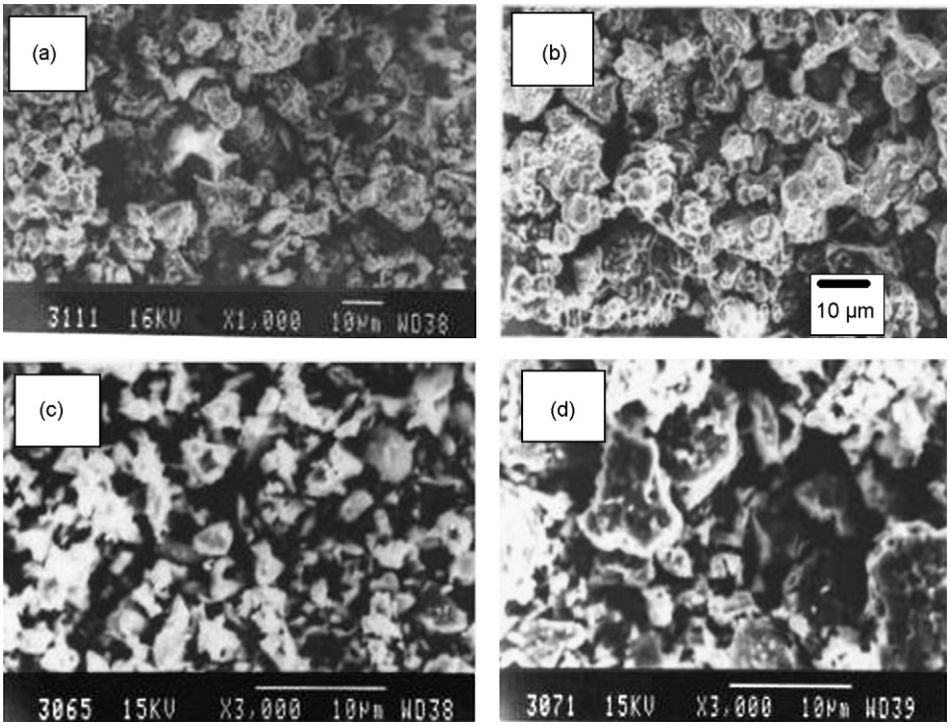

Fig. 13. SEM microstructures of the pellets sintered with different percentages of TiC: (a) and (b) carbothermic ZrB_2 powder, (c) & commercial ZrB_2 powder. (a) 5, (b) 30, (c) 5 and (d) 30 wt.% of TiC.

samples. This desintering effect that increased the porosity of composites with higher amount of TiC content can be due to combination of several reasons such as solubility of dispersoid phase to matrix or the vice versa, molar volume change during sintering, differential diffusivity of the phases [27]. It has been found that though the solubility of ZrB_2 is less into TiB_2 but TiB_2 has higher solubility in ZrB_2. It has been observed that when additive has more solubility into matrix phase the swelling can occur in the product. Also the change in molar volume during sintering due to some reaction product or the phase also leads to crack or pores due to stresses. The difference in the diffusivity of the two phases, segregation of phases can also lead to fragility and more pores during sintering. Considering all these, it was concluded that during high temperature sintering with higher percentages of TiC, formation of TiB_2 was observed. Some TiB_2/Ti must have gone into solution with ZrB_2, which has been observed in the SHS process by EDX analysis but no diffusion of Zr was observed into Ti containing grain. Also the molar volume of TiC (81.6) when gets converted to TiB_2 (25.6) during sintering at high temperature will lead to pore formation and swelling. Hence porous mass was obtained for the higher percentages of TiC addition.

The SEM microstructures of the fractured surfaces of sintered samples made from carbothermic and commercial powder is shown in Fig. 13. From the microstructures, it was apparent that very small amount of TiC was helping in sintering and the increase of TiC content led to segregation, porosity and less densification. The larger grain growth in pockets was also observed during sintering when segregation are there and normal grain growth took place similar to the normal sintering of ZrB_2 without any additive.

4. Conclusions

The effect of different amounts of TiC and C presence in the ZrB_2 matrix prepared by three different methods namely SHS, carbothermic and commercial powder was studied. The density was found to increase with the addition of C only upto 5 wt.%. Further increase in C content led to decrease in densification due to slow mass transport between the ZrB_2 grains and C does not take part in the sintering and stays at the grain-boundary. Out of all the three methods, the SHS process was best in terms of homogeneity of the sample the density could be increased from 87 to 94% of the theoretical density. It is believed that the smaller amount of carbon acted to reduce the surface oxygen of borides and led to enhancement of densification. In the case of TiC addition, it was observed that though there is increase in density with 5 wt.% TiC addition but the microstructure is not homogeneous. Further increase of TiC content leads to porous and inhomogeneous material in all the cases of ZrB_2 prepared by different routes. Formation of TiB_2 and TiB phase was observed for 10, 20 and 30 wt.% of TiC added samples. The porous structure was observed due to complex sintering and segregation during sintering.

Hence on the basis of the above studies, it is concluded that a very fine grained structure of the ZrB_2–C composite could be obtained with higher density by addition of 2–4% of C. Higher percentages of C are not beneficial to enhance the property in terms of sintering. TiC is not a good addition for sintering of ZrB_2, but the C additions in very small percentage (3–4 wt.%) can enhance the density drastically along with the control of grain growth. Composites prepared from SHS made ZrB_2 powder proved to give the most homogeneous product.

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