

# Effect of Silicon Carbide and graphite additives on the Pressureless Sintering mechanism and microstructural characteristics of Ultra-High Temperature ZrB<sub>2</sub> Ceramics Composites

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## ABSTRACT

The effect of SiC content, additives, and process parameters on densification and microstructural properties of pressureless sintered ZrB<sub>2</sub>- (1–10 wt %) SiC particulate composites have been studied. The ZrB<sub>2</sub>-SiC composite powders mixed by Spex mixer with 1-2wt% C (added as graphite powder) and CMC have been cold-compacted and sintered in argon environment in the temperature range of 1800–2100°C for 2hs. The amount of densification is found to increase with sintering duration and by prior holding at 1200-1650°C for reduction of oxide impurities (ZrO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) on powder particle surfaces via the formation of new phases such as ZrSi<sub>2</sub> and ZrC in the system. Presence of SiC with average size smaller than that of ZrB<sub>2</sub> appears to aid in densification by enhancing green density, increasing C content by erosion of milling media, and inhibiting matrix grain growth. Both of SiC and C appear to aid in reduction of oxide impurities. The shrinkage of samples was measured, and the microstructure of samples was examined using X-Ray Diffraction and scanning electron microscopy (SEM), equipped with EDS spectroscopy. Room temperature mechanical properties were examined. Sintering temperature has a great effect on relative density, porosity, water absorption, hardness, fracture toughness, oxidation resistance, Strength and microstructure of these composites. The highest relative density, (99.65%), was obtained in ZrB<sub>2</sub>-10wt. %SiC-2 wt. %C composites sintered at 2000°C for 2hs.

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## 1-Introduction

Zirconium diboride (ZrB<sub>2</sub>), an ultra-high temperature ceramic (UHTC) with melting temperature of 3250°C is of interest due to high electrical and thermal conductivities as well as

moderate density [1–4]. The density of ZrB<sub>2</sub> is lower than that of niobium-based refractory alloys, which requires protection against oxidation and ablation for aerospace applications. With addition of SiC as

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reinforcement to  $ZrB_2$ , its density and thermal expansion coefficient are further reduced, where as thermal conductivity, oxidation and ablation resistance as well as ability to retain strength at elevated temperature are significantly improved [1, 3, and 5]. This unique combination of properties makes the  $ZrB_2$  based materials attractive for various potential high-temperature thermal and structural applications at temperatures up to  $2000^\circ C$  [1,2], which include elevating-edges in hypersonic-entry type space vehicles, propulsion systems, furnace heating elements, refractory crucibles, and plasma-arc electrodes [2,5–8]. Processing of the  $ZrB_2$  from powdered raw materials to completely densified form is considered to be difficult, because of the covalent character of its bonding as well as lower magnitudes of both lattice and grain boundary diffusion rates. Therefore, densification of pure  $ZrB_2$  powder generally requires very high temperatures [9] ( $>2100^\circ C$ ) with moderate pressure ( $\sim 20\text{--}30\text{MPa}$ ), [10–12] or lower temperatures ( $\sim 1800^\circ C$ ) with extremely high pressures ( $>800\text{MPa}$ ) [13–14]. In recent years, significant attention has been devoted to pressureless sintering of the  $ZrB_2$  and  $ZrB_2$ -based composites, as this process is relatively inexpensive compared to hot pressing and offers the flexibility of near-net shaping of the finished products [15–31]. Densification of the pressureless sintered  $ZrB_2$  based materials can be more easily achieved by addition of SiC,  $B_4C$ , TiC or AlN in the form of reinforcement or additive, as reported recently [15-17].

Mallik et al. [18] has reported about the densification of  $ZrB_2$  and  $HfB_2$  based composites by pressureless sintering with addition of  $MoSi_2$ , which enhances the process of densification through formation of a borosilicate liquid film at matrix grain boundaries and particle–matrix interfaces. However, formation of such a film with low melting temperature at grain boundaries or interfaces is not desirable for elevated temperature applications. In contrast to the liquid phase formers, reactive agents such as  $B_4C$ , C, WC and VC combined with control of the sintering atmosphere, can be used to promote densification through solid state sintering by removal of surface oxides ( $ZrO_2$  and  $B_2O_3$  for  $ZrB_2$ ) [19–30]. In some of the reports [20–24, 29, 30], it has been shown that it is possible to

achieve relative density of  $>98\%$  through pressureless sintering of  $ZrB_2$  or  $ZrB_2$ -SiC composites using  $B_4C$  and C as additives. Furthermore, Yang. [24] Has demonstrated that it is possible to attain relative densities and mechanical properties comparable to those in the hot-pressed  $ZrB_2$  based composites by carrying out pressureless sintering of  $ZrB_2$  with 1–10 wt. % SiC reinforcement using  $B_4C$  and graphite as additives. Although WC has been reported to contribute to the process of densification of  $ZrB_2$  and  $ZrB_2$ -SiC composites [19, 20, 26, 27], the mechanisms proposed by the different investigators appear to be quite varied. It has been shown that WC is relatively less effective in reduction of surface oxides than  $B_4C$  and C [20] or VC in case of  $ZrB_2$  [26].

Based on preliminary studies by Balak et al. [29], it has been reported that the  $ZrB_2$ -SiC composites with higher reinforcement content show greater densification, indicating that besides the sintering additives, the SiC particles could have a role as well, which needs to be fully understood. The effect of SiC volume fraction on densification behaviour needs to be examined synergistically with that of additives and impurities with due emphasis on understanding of the operative mechanisms. Moreover, there is need to arrive at optimum temperature and duration of sintering, so as to obtain desired combination of relative density, microstructure and mechanical properties. Therefore, the present report is focused on studies comprising pressureless sintering of the  $ZrB_2$ -(2–10vol %) SiC composites at  $2000^\circ C$  for 2hs in order to examine the effects of C additive, as well as SiC content on their densification, matrix grain size, and mechanical properties.

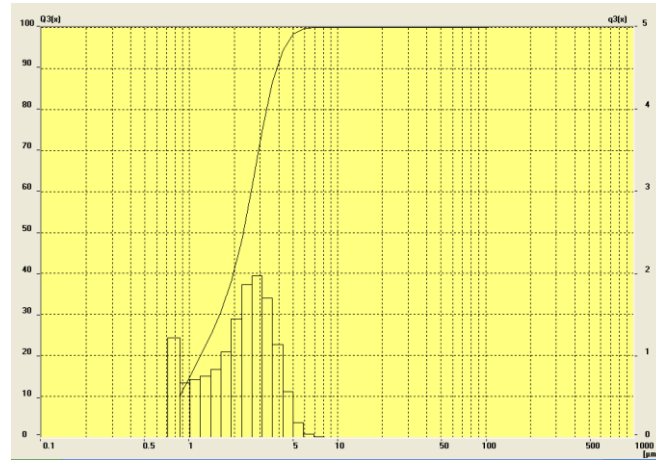
## 2- Experimental procedure

### 2-1- Materials and process

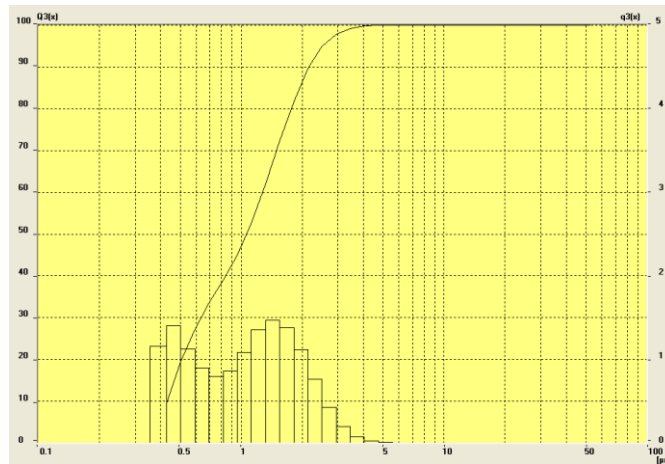
Commercially available powders of  $ZrB_2$ , SiC and C, each with 99.5% purity and less than  $2\ \mu m$  in size were used as raw materials in this study. The particle size of the powders was measured using the LPSA method, which are evident in Figures 1, 2 and 3. Powders of SiC and C were obtained from the merck Co., Germany, whereas the  $ZrB_2$  powder was purchased from the Global Co., China. For  $ZrB_2$ , a powder sample (ZBC) having compositions of  $ZrB_{2+}$  (2-10wt %) SiC+ (10wt %) CMC binder

was prepared, such that the carbon content was (1-2wt %) C. These samples were mixed using a Spex mixer (model Spex 8000, Glen Co., USA) operated at 250 rpm for 2hs. After the completion of milling, the blended powders were uniaxially pressed at 300MPa inside a steel die. The green compacts were pre-sintered in carbolite tube furnace (Carbolite Co., England) to 1400 °C at the rate of 10 °C /min, held there

for 1h, and were then sintered at 2000 °C in a high-temperature Linn High Therm furnace (Model GHV-200/200/2500 - Linn High Therm Co., Germany) having graphite heating element for time duration of 2hs under flowing argon gas followed by slow cooling down to room temperature. Fig. 4 illustrates the applied heating and cooling regime of sintered specimens.



**Fig. 1.** Particle size distribution of ZrB<sub>2</sub>.



**Fig. 2.** Particle size distribution of SiC.

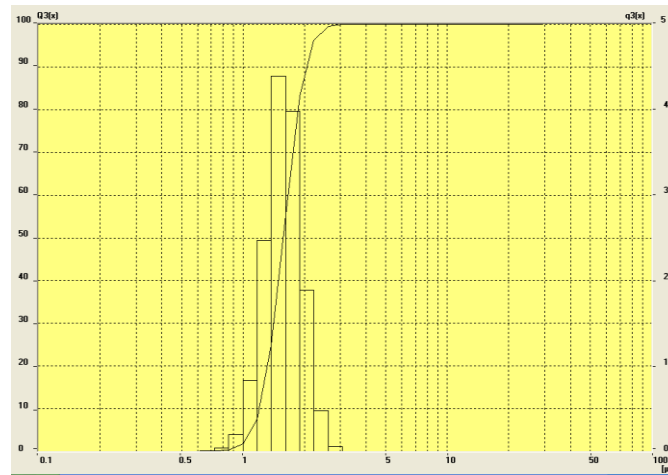


Fig. 3. Particle size distribution of Carbon.

## 2-2- Characterization of composites

The bulk density of each of the sintered samples was evaluated by Archimedes principle. Relative densities were calculated by normalizing the measured bulk density by the corresponding theoretical density. The sintered samples were initially polished sequentially on coarse and fine diamond-coated discs, subsequently on abrasive SiC papers. The different phases in the microstructures were also identified by XRD analysis (model Seisert-3003 PTS, made in Germany). The microstructures of these composites were examined by scanning electron microscopy (SEM, Cambridge, England) using both secondary electron (SE) and back scattered electron (BSE) imaging, whereas their chemical compositions were determined using energy dispersive X-ray (EDX) analyses.

As shown in Fig. 4, during the pre-sintering stage, in order to better removal of all the adhesives, as well as the inhibition of cracks formation, the heating rate was chosen at 10°C/min and maintained for one hour at 350°C. Then the temperature increased to 900°C, and kept at this temperature for one hour to prevent possible sample cracking. Thereafter, the furnace temperature reached 1400°C and the samples were kept at this temperature for one hour for pre-sintering of samples. In order to perform possible reactions during sintering, formation of desired phases such as ZrSi<sub>2</sub> and elimination of oxide impurities, samples were kept at 1650°C for one hour. Finally, sintering

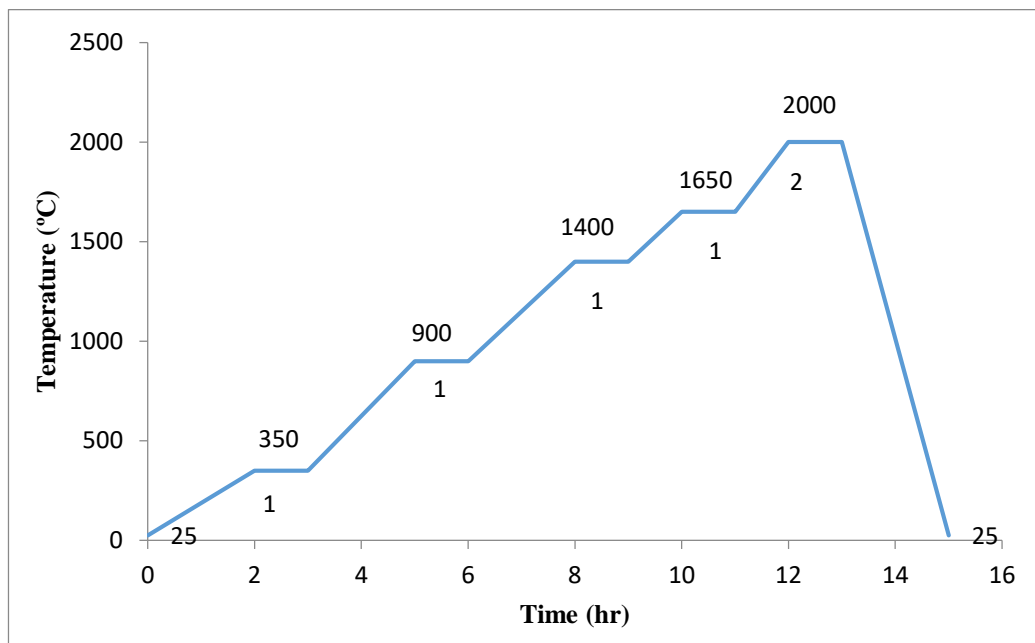
process was completed at 2000°C for 2hs [29-31].

## 3- Results and Discussion

### 3-1- Densification and evolution of microstructure

The variations of relative density of the sintered products as a function of the sintering temperature and SiC volume fraction for all the investigated sintered composites are shown in Tab. 1, Fig. 5 and Fig. 6, respectively. Analysis of the results in Fig. 5 indicates that the optimum temperature for achieving maximum relative density by pressureless sintering is 2000°C, while the values of relative densities of the composites sintered at 1800°C or 2100°C have been found to be less (Fig. 6).

However, the results of an earlier study on ZrB<sub>2</sub>-(1–10 wt %) SiC composites with 1 or 2 wt% C have not shown a definite manner of variation [24]. From the results shown in Fig. 5, the relative densities of the ZrB<sub>2</sub>-SiC composites are found to be >90% of the corresponding theoretical calculated densities, while that of the ZBC is only ~88%. Moreover, the values of relative densities are found to increase steadily with increase in volume fraction of SiC. These observations suggest that processing of completely dense pure ZrB<sub>2</sub> is very difficult, while the presence of SiC as reinforcement is significantly beneficial for promoting the process of densification.



**Fig. 4.** Applied heating and cooling regime for the samples.

In this study, maximum relative density of 99.65% was achieved in the ZS10C2 composite, which was sintered for 2hs after holding for 2hs at intermediate temperatures in 1650°C. The values of relative densities obtained in this study are comparable to those of the pressure-less sintered ZrB<sub>2</sub>-SiC composites, reported in previous studies [22, 24]. Following these studies, densification of ZrB<sub>2</sub>-SiC using pressureless sintering techniques were also investigated [31, 32]. It was found that a borosilicate liquid phase present on the particle surfaces had to be eliminated before the onset of

coarsening. B<sub>2</sub>O<sub>3</sub> on ZrB<sub>2</sub> and SiO<sub>2</sub> on SiC reacted to form a borosilicate liquid which promoted coarsening of the ZrB<sub>2</sub> grains. Reaction of carbon additives and combined carbon (such as SiC) with the borosilicate liquid, results in removing the liquid phase, and producing the near full density samples at sintering temperatures ranging from 1950-2000°C. This process produces ZrB<sub>2</sub>-SiC composites with mechanical properties similar to those obtained from hot pressing studies.

**Table 1.** Relative density of the sintered composite samples.

Sample	Sample Code	Measured density	porosity (%)	Water attraction (%)	Densification (%)
ZrB <sub>2</sub>	Z	5.0062	11.82	2.30	88.18
ZrB <sub>2</sub> -2%SiC	ZS2	5.2854	2.5	0.19	97.5
ZrB <sub>2</sub> -5%SiC	ZS5	5.1457	1.35	0.07	98.65
ZrB <sub>2</sub> -10%SiC	ZS10	4.7685	0.95	0.28	99.05
ZrB <sub>2</sub> -2%SiC-1%C	ZS2C	5.3469	1.75	0.02	98.25
ZrB <sub>2</sub> -5%SiC-1%C	ZS5C	5.0073	0.84	0.11	99.16
ZrB <sub>2</sub> -10%SiC-1%C	ZS10C	4.7567	0.48	0.29	99.52
ZrB <sub>2</sub> -10%SiC-2%C	ZS10C2	4.7154	0.35	0.24	99.65

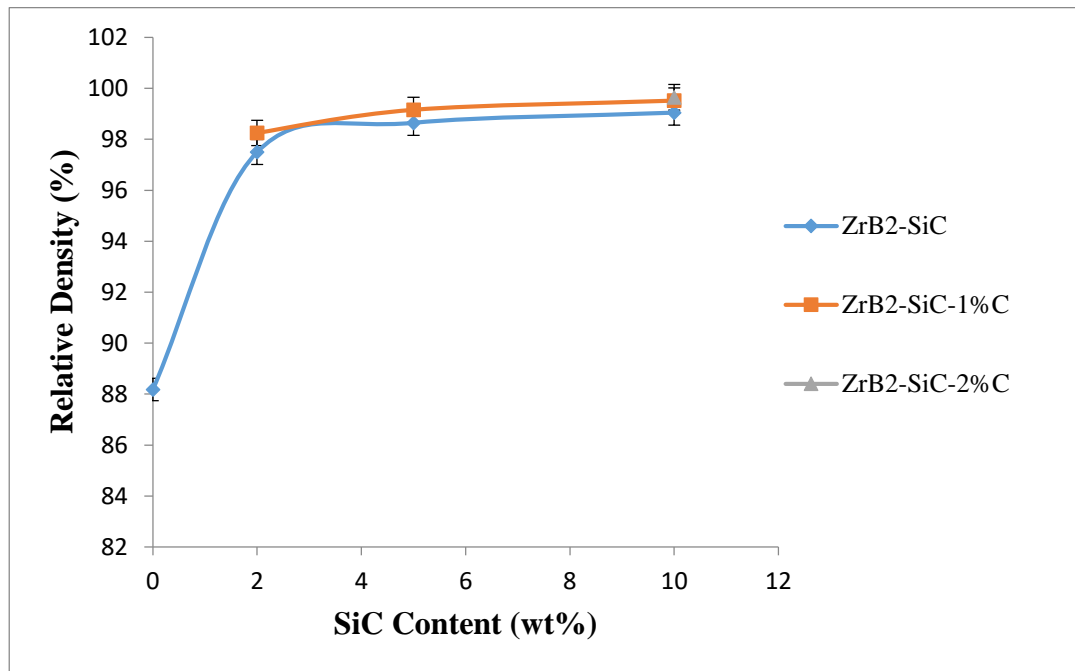


Fig. 5. The chart of relative density of the sintered composites as function of the SiC volume fraction.

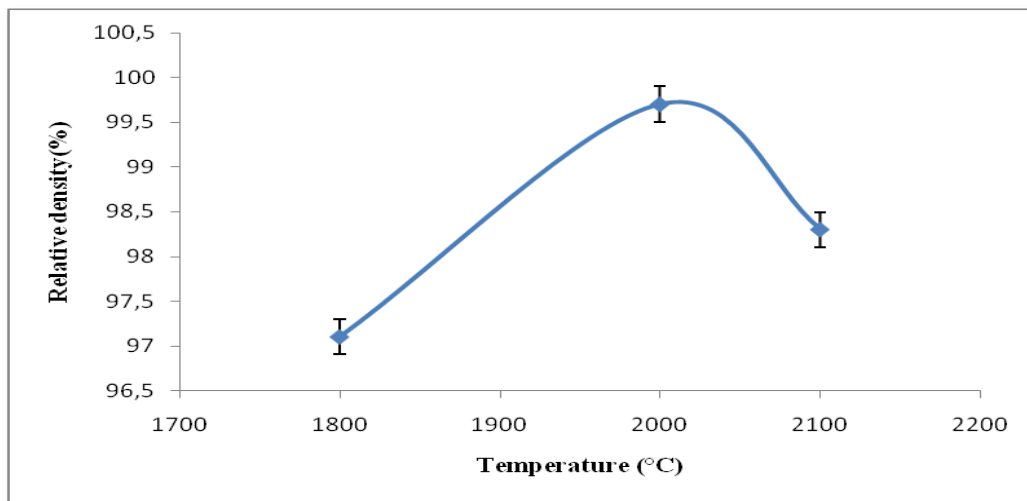


Fig. 6. Chart of the relative density of the sintered composites as a function of the sintering temperature for the ZS10C composite.

Typical XRD patterns depicting the peaks of the constituent phases in the microstructures of composite samples sintered at 2000°C for 2hs, are shown in Fig. 7. The X-ray diffraction (XRD) analysis of the used  $ZrB_2$  powder showed the peaks of  $ZrB_2$  in the XRD patterns. The peaks of SiC,  $ZrSi_2$ ,  $B_4C$  and C used as sintering additives are also observed for composite samples sintered in the recorded XRD patterns in this figure. The intensity of the XRD peaks of  $ZrSi_2$  and  $B_4C$  phases enhances with increasing

in SiC content in the composite powder mixtures after sintering, as shown in Fig. 7. The locations enriched in the aforementioned impurities within the microstructures of the sintered composites have been further investigated using SEM accompanied by EDX mapping. The results of bulk EDX analysis on the investigated composite samples have shown distinct evidence for the presence of  $ZrB_2$ , SiC and  $ZrSi_2$  in the sintered composites.

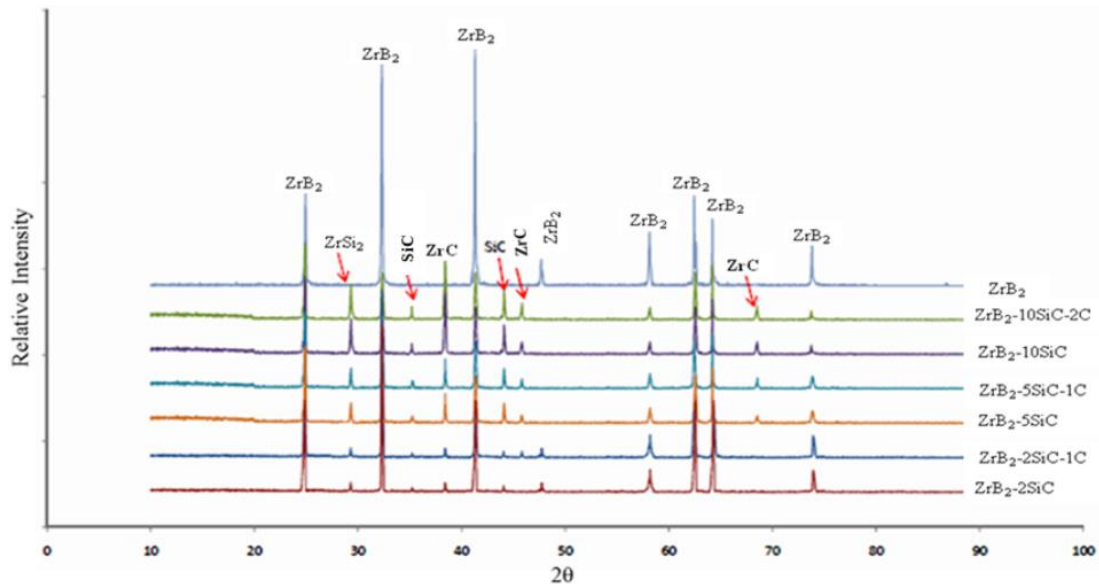


Fig. 7. Typical XRD patterns of composite samples sintered at 2000°C for 2hs.

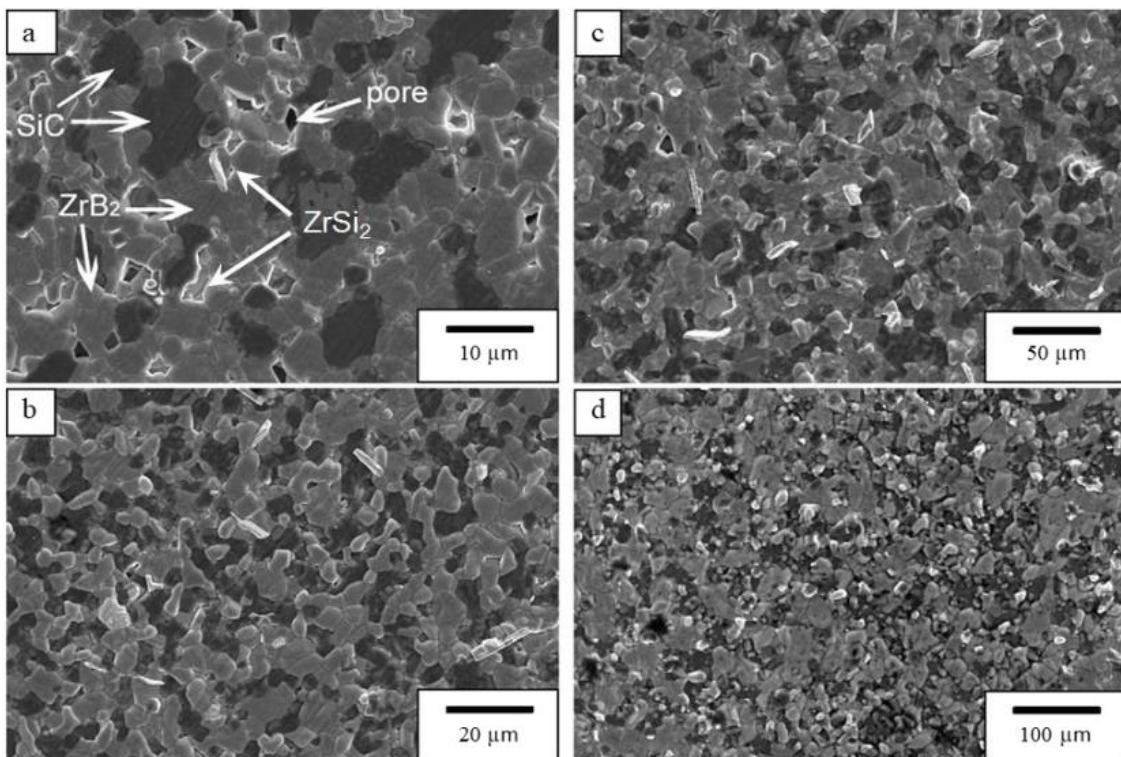


Fig. 8. SEM (BSE) images depicting the microstructures of ZS10C, obtained after sintering at 2000 °C for 2hs.

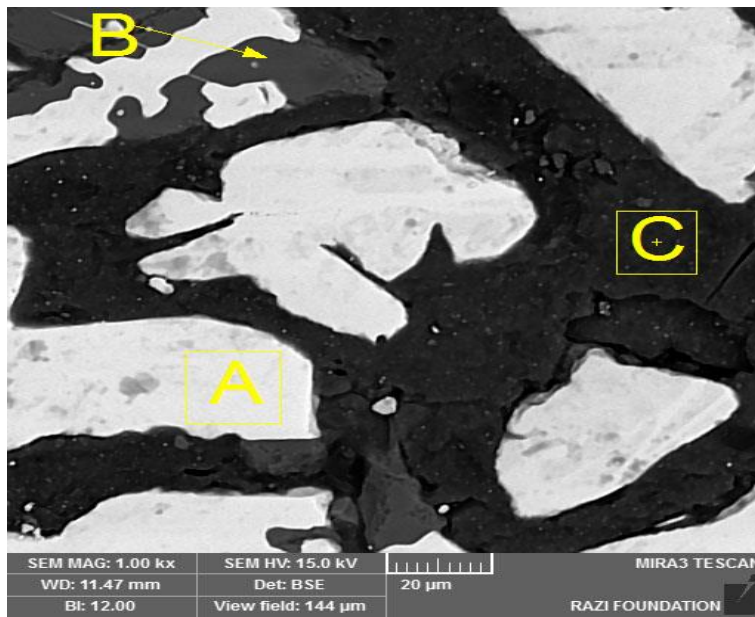


Fig. 9. SEM / EDS image of  $ZrB_2$ -10% SiC-1% C sample, obtained after sintering at 2000 °C for 2hs.

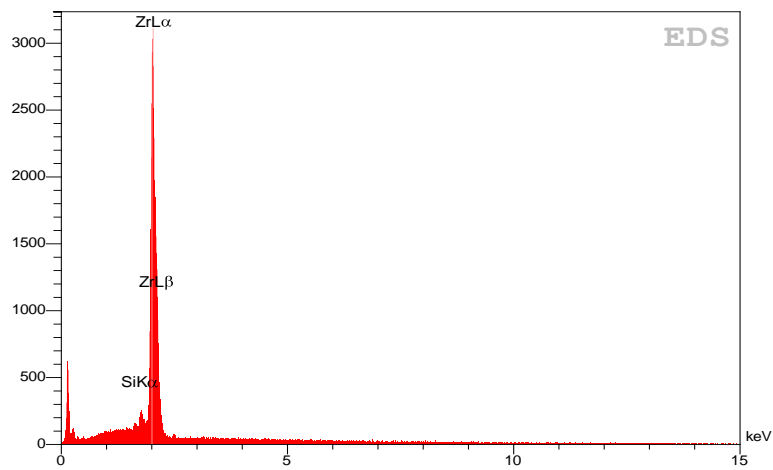


Fig. 10. Identified peak of phase A of  $ZrB_2$ .

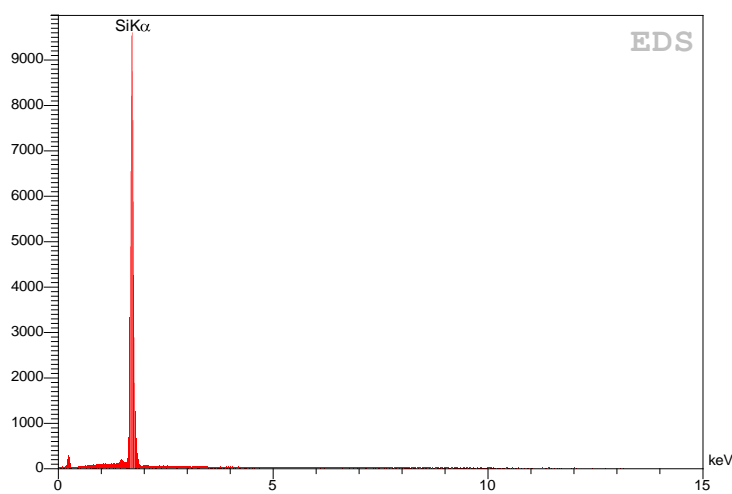


Fig.11. Identified peak of phase C of SiC.



The microstructures of ZS10C composites sintered at 2000°C for 2hs are shown with the SEM (BSE) images in Fig. 8(a) to (d), respectively. As expected, the contrast of different phases or locations in these SEM (BSE) images is found to depend on the average atomic numbers of the constituent elements. The identities of the major elements in each of these constituent phases have been confirmed by EDX analysis.

The microstructures and interfaces of all the investigated composites have been also examined at higher magnifications using SEM (BSE) imaging with EDX analysis, and the results are shown in Fig. 9. The SEM (BSE) images in this figure show the presence of an interfacial layer appearing relatively brighter than the ZrB<sub>2</sub> grains and forming a near-continuous network surrounding both matrix grain boundaries and particle–matrix interfaces. The locations appearing darker than SiC in Fig. 9 have been identified as either B<sub>4</sub>C or C through EDX analysis. In the Figure 9, the dark-colored parts are related to lighter molecules such as SiC and light-colored parts of heavy-phase regions, including ZrB<sub>2</sub>. Gray regions can also be related to possible intermediate phases such as ZrC.

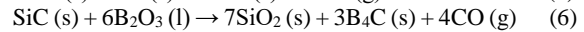
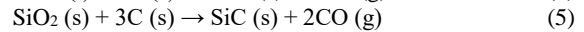
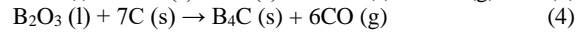
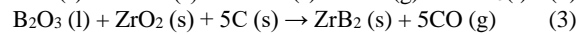
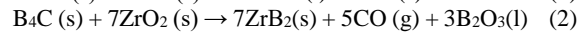
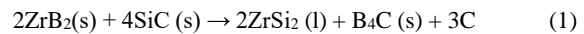
Regarding the peaks shown in Figures 10 and 11, phase A and C are related to ZrB<sub>2</sub> and SiC, respectively. The ZrSi<sub>2</sub> phase is a very small phase formed on the surface of the ZrB<sub>2</sub> grains, and given the fact that it is heavier than ZrB<sub>2</sub>, it is characterized by a clear aura around the ZrB<sub>2</sub> grains. Because the amount of ZrSi<sub>2</sub> is very low, it is not detected by the system. ZrSi<sub>2</sub> phase acts as the interstitial phase between SiC and ZrB<sub>2</sub>, obtaining Si from SiC and Zr from ZrB<sub>2</sub>, and serves as a sintering assistant phase in the systems, which strengthen grain boundary regions.

The added boron from ZrB<sub>2</sub> and C added from SiC can also appear as B<sub>4</sub>C, but as mentioned, this phase is not detectable by the system. The added carbon in the system reacts with ZrO<sub>2</sub> particles on the surface and restores them and appears as a ZrC phase [33- 36].

### 3-2- Thermodynamic Effect of additives and SiC on reduction of surface oxides

Addition of C is known to aid in the process of densification by reduction of the surface oxides [21, 23]. The temperatures used for pre-sintering

at intermediate temperatures of 1250°C and 1650°C were chosen through thermodynamic analysis of the following reduction reactions:



In this study, the aforementioned reactions (1–6) have been found during the process of sintering due to the loss of volatile reaction products. However, no definite trend has been observed in the variation of weight loss with either SiC content or temperature of sintering. Reaction (1) has been first proposed by Kagawa et al. [20], whereas reaction (2) and (3) have been suggested earlier by Zhang et al. [24] and Guo et al. [22].

Furthermore, through a more comprehensive study, reactions (2–5) have been suggested by Zhang et al. [24]. In addition, it has been shown by Zhu et al. [21] that combination of C additives is more effective in removal of surface oxides than these additives alone, as both ZrO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> are removed simultaneously. It has been shown that B<sub>2</sub>O<sub>3</sub> present in the powders used as raw materials, reacts with the SiO<sub>2</sub> present in the SiC powders to form borosilicate glass, which in turn promotes coarsening of the ZrB<sub>2</sub> grains, and there by the process of densification become complete [24,35]. By addition of C, the intergranular B<sub>2</sub>O<sub>3</sub> can be reduced through Reaction (3), and there by densification can be promoted. Therefore, the amount of densification in a given ZrB<sub>2</sub>–SiC composite has been found to depend on whether sufficient carbon is added in proportion to the net oxygen content of the raw materials [24].

Through analysis of thermodynamic data, it is observed that reaction (6) is feasible at temperatures >1750°C. This suggests that the SiC particles present as reinforcement or those formed by reaction (5) contribute to the process of densification at the sintering temperature by removal of B<sub>2</sub>O<sub>3</sub>. It is intuitive that increase in SiC volume fraction increases the net ZrB<sub>2</sub>–SiC interfacial area, which in turn promotes reaction (6) at the sintering temperature causing the removal of B<sub>2</sub>O<sub>3</sub>, and there by leads to densification.

Therefore, in the present study, based on the micro structural observations pertaining to the  $ZrB_2$  grain boundaries, it is appropriate to infer that a limited amount of liquid phase is formed at a significant fraction of the matrix grain boundaries and  $ZrB_2$ -SiC interfaces during sintering of the investigated composites, and enhanced diffusion through this liquid could have contributed to the process of densification.

The composites fabricated by pressureless sintering in this study have been found to retain their structural integrity in spite of their exposure to temperatures  $>2000^\circ\text{C}$  at the tips of oxyacetylene flame [30], which suggests that these materials are stable at elevated temperatures in spite of impurity segregation at a fraction of the interfaces.

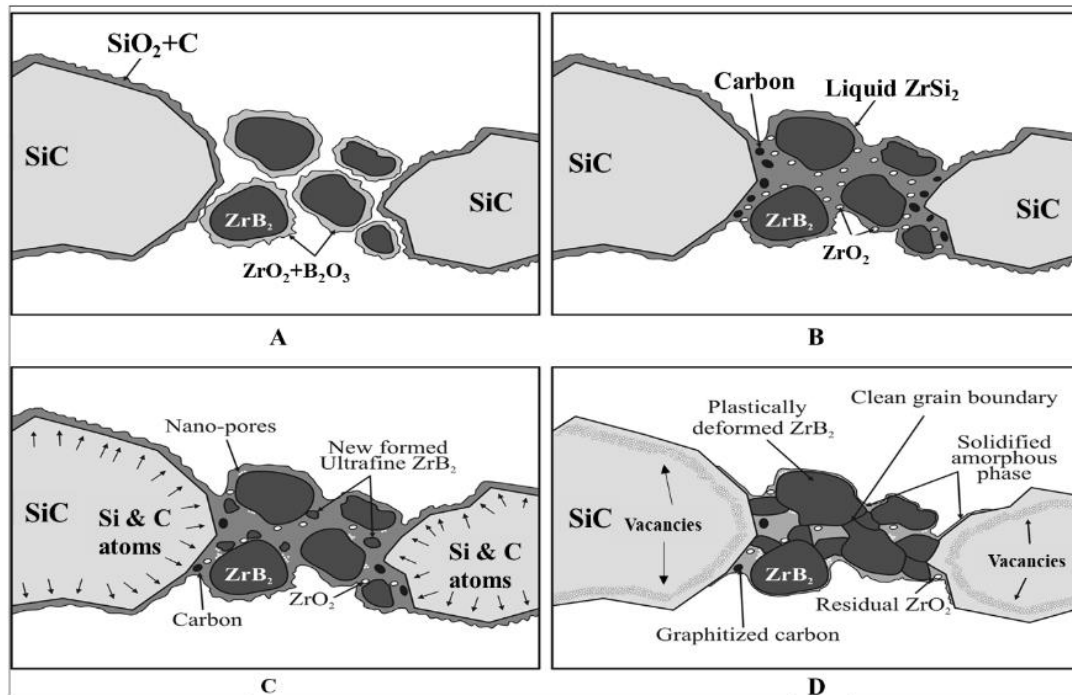


Fig. 12. Schematic view of sintering mechanisms in  $ZrB_2$ -SiC system.

The above figure shows a schematic of how to combine  $ZrB_2$  and SiC particles during the sintering process. As shown in Fig 12-a,  $ZrO_2$  and  $B_2O_3$  oxide impurities are observed on the surface particles of  $ZrB_2$  as well as  $SiO_2$  and free carbon on the surface of SiC particles. The formation of an interfacial liquid  $ZrSi_2$  phase between the particles and floatation of other surface impurities in it, in Fig 12-b is clear (equations (1)). The formation of  $ZrB_2$  particles through chemical reactions (equations (3) and (4)) and the emission of carbon / silicon particles of SiC particles to surfaces that create a vacancies layer in the SiC grains behind the interface are shown in the fig 12-c. Finally, neck formation between the grains, plastically deformation of main  $ZrB_2$  particles and solidification of pores and particles containing interfacial layer, were obtained (Fig 12-d) [19].

According to the above and the formation of the  $ZrSi_2$  phase at  $1620^\circ\text{C}$ , the main mechanism of sintering process, is liquid phase sintering. Of course, due to the formation of the  $ZrC$  phase during the sintering process in  $ZrB_2$ -SiC composite samples, solid-state sintering is also not expected.

#### 4. Conclusions

The following conclusions can be drawn based on the studies related to pressureless sintering of  $ZrB_2$ -SiC composites with C (added as graphite) as additives:

- The use of C as sintering additives promote densification by reduction of the oxide impurities comprising  $ZrO_2$  and  $SiO_2$  in the powder mixture used as raw material.
- Relative densities of sintered products are found to increase with increasing the volume

fraction of SiC particles. The presence of SiC is also beneficial for densification during sintering, because it participates in reducing  $B_2O_3$  and  $SiO_2$  at the  $ZrB_2$ -SiC interfaces, restricting grain growth.

- Microhardness of the composites is found to increase with duration of sintering for 2hs depending on their composition due to increase in relative density of the investigated composites. With further increase in the temperature of sintering, hardness is found to decrease due to grain growth.

- According to the sintering results, the main mechanism of sintering process, is liquid phase sintering. Of course, due to the formation of the ZrC phase during the sintering process in  $ZrB_2$ -SiC composite samples, solid-state sintering is also not expected.

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