Development of ZrB$_2$–SiC–Ti by multi stage spark plasma sintering at 1600°C

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Zirconium diboride based ceramics, owing to their superior high temperature properties are potential materials for use as leading edge components in hypersonic space vehicles. However, the difficulty in sintering these ultra high temperature ceramics limits their applications to some extent. Sintering of such materials is usually accomplished by resorting to advanced sintering techniques such as Spark Plasma Sintering (SPS) accompanied by sinter aids to improve the sinterability. In this backdrop, the current work investigates the effect of Ti addition on the mechanical properties and sinterability of ZrB$_2$–based ceramic composites. Tailored addition of Ti to ZrB$_2$–18 wt.% SiC baseline composites not only improves the densification but also increases hardness and indentation toughness, when sintered using Multi Stage Spark Plasma Sintering technique. Microstructure and X-ray diffraction analysis reveals the presence of ultrafine grains of ZrB$_2$ and SiC, which is found to be effective in obtaining a good hardness (up to 29 GPa) and reliable indentation toughness (up to 9 MPa·m$^{-1/2}$).

Key-words : Spark plasma sintering, Zirconium diboride, Titanium, Microstructure, Mechanical properties, Coupled thermostructural analysis

1. Introduction

Hypersonic space vehicles are subjected to extreme pressure and heat flux due to shock induced loading. The highly thermal load intensive trajectories for hypersonic space vehicles require the base materials to sustain operating temperatures in the range of 1600–2400°C, to resist evaporation, erosion, oxidation as well as to maintain mechanical integrity. Ultra high temperature ceramics (UHTCs) are suitable for such applications as they have high melting point, hardness, wear resistance and are chemically inert. In particular, the low density, low volatility and high thermal and electrical conductivity of Zirconium diboride (ZrB$_2$) among the different UHTCs make it most suitable for such applications. But UHTCs, like ZrB$_2$ are difficult to consolidate due to high melting point, low self-diffusion coefficient and presence of oxide layer on the powder particles. The sintering of ZrB$_2$–based ceramics with SiC as an additive has been studied in detail by many researchers. Gupta et al. investigated the effect of TiSi$_2$ addition on ZrB$_2$–SiC based ceramics and compared the effect of various SPS schemes like single stage, two stage and multi stage sintering on the mechanical properties. Rezaie et al. studied the oxidation behaviour of ZrB$_2$–SiC and proposed its oxidation mechanism at temperatures up to 1500°C. Zhang et al. have reported reactive hot pressing of ZrB$_2$–SiC composites with maximum densification of 97% and hardness of 21 GPa. The oxidation resistance of fully dense ZrB$_2$ with TaB$_2$ and TaSi$_2$ additives has been investigated, which showed that TaSi$_2$ is more effective as an additive than TaB$_2$. The fabrication of ZrB$_2$–based ceramics with SiC whisker reinforcement by spark plasma sintering and hot pressing has showed improvement in mechanical properties as compared to monolithic ZrB$_2$. The effect of ZrC addition has been investigated by Medrì et al. and MoSi$_2$ by Takashi et al. The pressureless sintering of ZrB$_2$ with ZrO$_2$ as additive was investigated by Mukhopadhyay et al. A similar study investigated the effect of ZrO$_2$ addition on mechanical properties of ZrB$_2$ composite and reported high hardness (14 GPa) and fracture toughness (11 MPa·m$^{-1/2}$).

The addition of metallic sinter aids to ZrB$_2$ has also been reported by a few research groups. For example, the effect of addition of Molybdenum has been investigated by Wang et al., but near theoretical densification has not been reported. Similarly, the addition of Niobium has been investigated by Sun et al., where near theoretical densification with maximum hardness of up to 16 GPa has been reported. Ni addition to monolithic ZrB$_2$ has been reported with incomplete densification and fracture toughness of only 3.4 MPa·m$^{-1/2}$. Also, Cu addition to ZrB$_2$ has been attempted and the hardness of 19 GPa and fracture toughness of 7.5 MPa·m$^{-1/2}$ has been reported. An important criterion for material selection pertaining to aerospace applications is to minimize weight, so the higher densities of Niobium (8.57 g/cc) and Molybdenum (10.2 g/cc) can put limits on their use owing to weight restrictions/penalty. Hence, a metal with lower density like Titanium (4.51 g/cc) is much more favourable as an additive for improving properties of ZrB$_2$–based ceramics.

Conventional sintering methods like hot pressing or reactive hot pressing, can be used to obtain ZrB$_2$ with hardness values in the range of 14–27 GPa and indentation toughness in the range of 2.1–4.6 MPa·m$^{-1/2}$, but only at sintering temperatures greater than 1750°C. Further improvement in toughness and hardness, in congruence with lowering of sintering temperature requires more
advanced sintering techniques. Recently many researchers have reported the use of Spark Plasma Sintering (SPS) for development of ZrB2-based ceramics. SPS provides an edge over conventional sintering techniques as it provides higher heating rates, shorter holding times and lower sintering temperatures. SPS technique has enabled the lowering of sintering temperature required to consolidate UHTCs, as well as control grain growth and formation of secondary phases simultaneously. However, conventional SPS technique with single step heating to the sintering temperature has a drawback, namely development of temperature gradients across the sample cross-section, which not only degrades the mechanical properties but also limits the size of sample that can be sintered. It has been reported that with single stage SPS, sintering temperature in excess of 2000°C is required to attain hardness greater than 20 GPa, but with indentation toughness of only 3.5 MPa m^{1/2}. Single stage spark plasma sintering of ZrB2 with Carbon Nanotubes has been investigated, but densification and mechanical properties are lower compared to ZrB2–SiC composite. Similarly, single stage spark plasma sintering of ZrB2 with graphene reinforcement has also been attempted, but densification and mechanical properties lower than that of monolithic ZrB2 have been reported. This shows that single stage SPS has limited advantage. Recent investigations on multi stage sintering (MSS) for a variety of ceramics has yielded considerably better results in terms of microstructure and mechanical properties. In MSS, the sample is held at intermediate temperatures for fixed duration before holding at the final sintering temperature. This enables homogeneous densification without microstructural coarsening and results in uniform mechanical properties, for both conducting as well as non-conducting ceramics. In this perspective, the current work investigates the use of Multi Stage Spark Plasma Sintering (MS-SPS) for developing ZrB2–18 wt. % SiC composite ceramics with Ti as a novel metallic additive. A range of weight percentages of Ti have been added to ZrB2–18 wt. % SiC ceramic to determine the optimum composition for developing high performance ZrB2–based ceramic material at lower sintering temperature with high density and superior mechanical properties.

2. Experimental details

2.1 Material processing

Commercially available powders of ZrB2 (purity 99%, D50, 1 μm, Nanoshel, USA), SiC (purity 99%, D50, 1 μm, Nanoshel, USA) and Ti (purity 99%, D50, 1 μm, Nanoshel, USA) were used as starting materials. X-ray diffraction (XRD) analysis of starting powders was carried out using Cu Kα radiation (λ = 1.54 Å) to confirm the phase purity and ascertain the presence of any secondary phases. The powders corresponding to three different compositions, viz. ZrB2–18 wt. % SiC–x wt. % Ti (x = 0, 5 & 10) were mixed by wet ball-milling (toluene medium) at 300 rpm for 8 h in a Tungsten Carbide (WC) jar with ball to powder ratio of 10:1. The milled powders were dried in an oven and then placed in a graphite die of inner diameter 15 mm, lined with graphite sheet. The graphite die containing the powder fitted with punch was placed inside the SPS chamber for sintering. The sintering of all the three compositions were carried out using multi stage sintering route, as shown in Fig. 1. For this, SPS experiments (Dr. Sinter, Model 515S, SPS Syntax Inc., Japan) were conducted in vacuum at three different holding temperatures viz., 1400°C, 1500°C and finally at 1600°C, with a holding time of 5 min at each stage. During the sintering, the temperature was monitored and regulated by an optical pyrometer. The powder compact was maintained under uniaxial pressure of 30 MPa during the course of the sintering cycle. The shrinkage of the powder compact was monitored by a dilatometer to ascertain the densification behaviour of the ceramic compositions. After final stage of sintering, the power was turned off and the powder compact was allowed to cool naturally in the vacuum chamber.

2.2 Determination of multi stage sintering scheme

Multi stage sintering was selected over single stage sintering as it offers numerous advantages like improvement in densification, mechanical properties, homogeneous and uniform microstructure development. The temperatures for different holding stages during MSS need to be selected carefully according to the melting temperature (Tm) of the base ceramic (ZrB2). In our research group, Reddy et al. employed holding temperatures of 0.45Tm, 0.50Tm, 0.55Tm for Al2O3. Jain et al. used holding temperatures of 0.40Tm, 0.45Tm, 0.52Tm for TiB2 and Gupta et al. used holding temperatures of 0.40Tm, 0.46Tm, 0.50Tm for ZrB2 to achieve highly densified ceramics with fine grain sizes. Based on the previous experience and considering the melting point of ZrB2 (3040°C), holding temperatures of 0.45Tm, 0.50Tm, 0.53Tm were selected for our ZrB2–SiC–Ti ceramics, as shown in Fig. 1. In our understanding, first holding at 1400°C would enable electric discharge induced surface activation, second holding at 1500°C would facilitate grain boundary diffusion induced neck growth formation and final holding at 1600°C would aid in complete densification of ceramic by plastic deformation of Ti additive which has melting temperature of 1668°C.

2.3 Microstructural characterization & mechanical properties

The densities of the sintered ceramics were measured using Archimedes method in acetone. The theoretical densities of ZrB2 compositions were calculated following rule of mixtures, by considering the densities of ZrB2, SiC and Ti as 6.09, 3.21 and 4.51 g/cc respectively. The phase analysis of the sintered composites was carried out using XRD. The microstructural features of the sintered ceramic composites were obtained using Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS) (Ultra 55, Carl Zeiss) operated at 20kV. The sample preparation for SEM was done by polishing with emery papers (up to # 2000) followed by polishing with diamond paste (2, 1 and 0.25 μm grades) to obtain mirror finish. The samples were further polished with colloidal silica before chemically etching with 10:1 (by volume) HCl:HNO3 solution for 5 min. The hardness was measured using Vickers indentation method.
(Zwick UTM, Germany) with a diamond indenter (apex angle of 136°). The Vickers hardness was estimated with a load of 2 kg (dwell time 15 s). The hardness value was calculated from indentation size using Eq. (1).\(^{35}\)

\[
H_v = 1.854 \left( \frac{P}{d^2} \right)
\]

(1)

where \(P\) is indentation load and \(d\) is mean length of indent diagonal. The reported values of hardness were calculated from at least six indentation tests on each sample. The fracture toughness of the composites were estimated using the indentation toughness method with the same indenter but at a higher load of 50 kg, so as to induce cracks at the indent tip. The length of the crack was measured using SEM and the model proposed by Anstis et al.\(^{36}\) represented by Eq. (2) given below was used to estimate the indentation toughness \((K_i)\).

\[
K_i = 0.016 \left( \frac{E}{H} \right) \left( \frac{P}{c^{1/2}} \right)
\]

(2)

where \(E\) is the Young’s Modulus, \(H\) is the Vickers hardness, \(P\) is the indentation load and \(c\) is semi-crack length. Multiple indents at different radial locations on the sintered ceramic were made and at least four estimates were made for more reliable measurement.

3. Results and discussion

3.1 Sintering behaviour

Shrinkage behaviour of ZrB\(_2\)-18 wt. % SiC-x wt. % Ti during MS-SPS for sintering temperatures of 1400°C, 1500°C and 1600°C have been evaluated (see Fig. 2). The shrinkage of powder compact occurs slowly during the first holding time of 5 min at 1400°C whereas shrinkage rate increases during second holding time of 5 min at 1500°C. But, shrinkage becomes more aggressive at the final holding of 1600°C and the ceramic continues to shrink till the end of final holding time of 1600 s. This shrinkage behaviour has been observed for all three ceramic compositions, thus establishing the suitability of holding times of 5 min at each stage of MS-SPS. The positive effect of Ti addition on the ceramic compaction is quite evident with shrinkage rates being higher, particularly during first and second holding times for 10 wt. % Ti and 5 wt. % Ti addition as compared to ZrB\(_2\)-SiC base composition. Maximum shrinkage for ceramic without Ti addition occurs towards the end of final holding stage, whereas shrinkage achieves saturation in case of 5 and 10 wt. % Ti addition.

Figure 3 shows the variation of SPS heating current with time. It can be observed that current aggressively increases just before each holding stage and thereafter decreases, followed by stabilization for the remaining period of the holding stage. Depending on the electrical conductivity of the powder compact, the current can flow either through graphite die wall or the powder compact. But owing to higher electrical conductivity of ZrB\(_2\), the major fraction of the current in the present case would flow through the powder compact. It is known that the neck formation occurs in the initial stage, which is followed by neck growth leading to continuous pore channel formation during the intermediate stage of sintering. The stabilization of electric current leads to controlled mass transport around neck regions caused by uniform spark discharge behaviour during these intermediate stages. Hence, it is quite plausible that in case of multi stage SPS, surface activation by electrical pulses as well as neck formation occurs in the first stage, followed by uniform neck growth during second holding and elimination of remaining closed pores during the final holding stage. During the MS-SPS schedule, such holding periods are experienced by the powder compact thrice as compared to only one time in case of SSS, which is believed to be one of the factors affecting uniform densification behaviour observed in the case of MS-SPS.\(^{30}\)

3.2 Densification behaviour

The shrinkage of the powder compact during the SPS process was used to evaluate the densification behaviour during the sintering process. These shrinkage curves with respect to temperature were recorded for ZrB\(_2\)-18 wt. % SiC composites, with different wt. % of Ti (0, 5 & 10) during multi stage sintering process. The densification behaviour during the SPS process has been quantified using densification parameter (\(\Psi\)), which is defined as,

\[
\Psi = \frac{\rho_f - \rho_i}{\rho_{fb} - \rho_i}
\]

(3)

where \(\rho_f\) is instantaneous density, \(\rho_i\) is the initial density, and \(\rho_{fb}\) is the final density.
is the theoretical density of ceramic composite. Figure 4 depicts the variation of Ψ with respect to sintering temperature. In the absence of Ti, densification began at around 1336°C (onset temperature), while it started at 1260°C for 5 wt. % Ti addition and 1150°C for 10 wt. % Ti addition. This clearly indicates that Ti addition promotes densification at an early stage of sintering. The reasons for such effect of Ti are presently under investigation, but it is believed that in the temperature range under consideration, Ti perhaps undergoes plastic deformation and enables rearrangement of powder particles under the uniaxial load during SPS. In addition, the formation of transient liquid during sintering (melting temperature of Ti is 1668°C34)) perhaps has resulted in liquid phase assisted sintering to enhance densification.

The addition of Ti enables appreciable early shrinkage with initial rise in liquid phase assisted sintering to enhance densification of powder particles under the uniaxial load during SPS. The inherent refractory nature of the sintering reaction medium. The inherent refractory nature of the sintering reaction products re-forms the presence of oxide impurities on the densification behaviour.

A careful analysis of Fig. 6 indicates the additional presence of ZrSi2, TiSi2, TiC and small traces of ZrC and TiO2 as sintering reaction products, along with WC contamination from the milling media. The inherent refractory nature of the sintering reaction products reflect on the occurrence of high temperature sintering reactions. It may also be observed that metallic Ti additive is not detected within the detection limits of the diffractometer, thereby implying full consumption of Ti phase in formation of the sintering reaction products. It is worth mentioning here, that the formed secondary phases are refractory in nature and are expected to enhance the properties of the developed ceramic composites. A comparison of XRD patterns of sintered ceramics.

Table 1. Densification data and mechanical properties of ZrB2–based ceramics, which were spark plasma sintered at 1600°C for 5 min, 30 MPa and with heating rate of 100°C/min in vacuum atmosphere (*Theoretical density estimated using starting composition only)

| Material composition (in wt. %) | Theoretical density* (ρt, g/cc) | Sinter density (ρs, g/cc) | Vickers hardness (Hv, GPa) | Indentation toughness (Kt, MPa m1/2) |
|---------------------------------|---------------------------------|--------------------------|---------------------------|-----------------------------------|
| ZrB2–18SiC–0Ti                  | 5.20                            | 5.10                     | 17.5 ± 0.9                | 3.7 ± 0.7                          |
| ZrB2–18SiC–5Ti                  | 5.16                            | 5.20                     | 20.4 ± 0.8                | 5.6 ± 0.5                          |
| ZrB2–18SiC–10Ti                 | 5.09                            | 5.10                     | 29.2 ± 2.0                | 9.0 ± 0.9                          |

Fig. 4. Densification parameter (Ψ) vs. temperature for ZrB2–18 wt. % SiC–x wt. % Ti (x = 0, 5 & 10) samples sintered using MS-SPS with heating rate of 100°C/min and applied pressure of 30 MPa.

3.3 Phase stability and thermodynamic analysis of sintering reactions

X-ray diffraction patterns recorded with the starting powders, as well as the spark plasma sintered samples are depicted in Figs. 5 and 6 respectively. It can be observed that the starting powders of ZrB2 and SiC contain small amount of oxide impurities in the form of ZrO2 and SiO2, since the procured powders are stated to be 99% pure and thus have impurities <1% comprising of metallic and non-metallic elements. Titanium powder conforms to its high purity, with no secondary phase within the detection limit of XRD. It is a known fact that as with other Boron containing ceramic powders, ZrB2 powder has a ubiquitous surface layer containing oxide impurities (ZrO2 and B2O3).37) Oxygen impurities (B2O3 and ZrO2) present on the starting powder surfaces have been shown to inhibit densification and promote grain growth in the non-oxide ceramic systems.38) In the present study, the ZrB2–SiC–Ti ceramic compositions sintered using MS-SPS scheme are found to be fully dense, as detailed in Section 3.2 and we have observed the absence of any detrimental effects of the oxide impurities on the densification behaviour.
with starting powders brings out an increase in the relative intensities of ZrO2 in the sintered ceramics. This is attributed to the presence of a thin protective micro-layer of oxide on Titanium powders.39)

Following the XRD analysis, the thermodynamic feasibility of the possible sintering reactions leading to the formation of sintering reaction products have been analyzed and the following feasible reaction has been identified.

$$2\text{ZrB}_2 + 5\text{SiC} + 7\text{Ti} + 3\text{SiO}_2 + \text{ZrO}_2$$
$$\rightarrow \text{TiSi}_2 + 3\text{ZrSi}_2 + 5\text{TiC} + \text{TiO}_2 + 2\text{B}_2\text{O}_3$$

The Gibbs free energy change ($\Delta G$) for the proposed reaction has been calculated and plotted as a function of temperature in Fig. 7. It can be seen that the reaction is thermodynamically feasible throughout the sintering temperature range with a $\Delta G$ of $-310.2 \text{kJ}$ at 1600°C. It may be mentioned here that B$_2$O$_3$, as observed in the reaction, vapourizes rapidly above 1127°C and hence was not detected after sintering above 1400°C.40) An additional reaction pathway is proposed by considering ZrC as one of the sintering reaction products.

$$2\text{ZrB}_2 + 3\text{SiC} + 4\text{Ti} + 3\text{SiO}_2 + \text{ZrO}_2$$
$$\rightarrow 2\text{TiSi}_2 + \text{ZrSi}_2 + 2\text{ZrC} + \text{TiO}_2 + 2\text{B}_2\text{O}_3$$

Gibbs free energy change for the above reaction indicates its feasibility above 1460°C, as seen in Fig. 7. The SPS process has been conducted in the temperature range of 1400–1600°C. It needs to be mentioned here that in the present work, as well as in most of the SPS related literature, the temperature during SPS is measured by focusing an optical pyrometer on the outer surface of a graphite die, which invariably ignores the temperature gradient from the sample centre to the outer surface.41) It has been reported that, in general, the difference between actual sample temperature and outer surface of graphite die is $\approx 100{ }^\circ\text{C}$ or higher.42) In this backdrop, we believe that the ZrB$_2$ powders contained in the graphite die actually experience a higher temperature than the pyrometer reading. Hence, from the free energy data, it can be expected that the latter reaction is also likely to take place, particularly during MS-SPS holding stages at 1500°C and 1600°C.

### 3.4 Microstructure characterization

The microstructural investigation of the SPSed ZrB$_2$–SiC–Ti samples have been performed after chemically etching the polished samples. The grain size distribution and the atomic contrast among the different phases are apparent in the back scattered electron microscopy (BSE-SEM) image, as seen in Fig. 8(1). It can be seen that the darker grains of SiC are spread in a lighter ZrB$_2$ matrix. The brighter spots in the micrograph corresponds to WC contaminants introduced from the milling media. The exclusive presence of individual sintering reaction products viz., ZrSi$_2$, TiSi$_2$, TiC, etc. have not been clearly identified, as it requires careful transmission electron microscopy (TEM) in order to study the finer microstructure.
scale microstructure. The presence of inhomogeneous irregular shaped ZrB$_2$ grains in some regions of the microstructure presents evidence for the occurrence of liquid phase sintering. Grain size measurements have been carried out using ImageJ software considering circular and elliptic fit of the grains, which shows average grain size of 2.4 ± 0.3 μm for ZrB$_2$ grains with mean aspect ratio of 1.5 ± 0.2 and average grain size of 2.2 ± 0.6 μm with mean aspect ratio of 1.9 ± 0.2 for SiC grains. The present grain size shows no exorbitant grain growth, which supports the observed improvement in the mechanical properties.

Energy Dispersive Spectroscopy at selected locations reveals clearly the presence of ZrB$_2$ [Fig. 8(2)] and SiC grains [Fig. 8(3)]. Regions with Ti (light grey contrast) at selected locations are seen to be accompanied by C and Si indicating that it is in a combined state in the microstructure as TiSi$_2$ and TiC [Fig. 8(4)], while Fig. 8(5) shows the presence of WC. Elemental mapping has been carried out using EDS essentially to map the distribution of Zirconium (line K$_\alpha$ at 2.040 keV), Silicon (line K$_\alpha$ at 1.739 keV), Carbon (line K$_\alpha$ at 0.266 keV), Titanium (line K$_\alpha$ at 4.51 keV) and Oxygen (line K$_\alpha$ at 0.517 keV). The BSE-SEM image [Fig. 9(1)] and the corresponding elemental distribution of Zirconium [Fig. 9(2)], Silicon [Fig. 9(3)], Carbon [Fig. 9(4)], Titanium [Fig. 9(5)] and Oxygen [Fig. 9(6)] obtained by EDS, confirms the elemental constituents present in the sintered ceramics. Boron has not been mapped because being a light element, it is at the detection limit of the spectrometer. Moreover, its K$_\alpha$ line (at 0.172 keV) severely overlaps with the M$_\alpha$ line of Zr (at 0.152 keV), thus introducing an unnecessary uncertainty into the measurements.43)

3.5 Mechanical properties

The mechanical properties including Vickers hardness and indentation toughness of ZrB$_2$–SiC–Ti ceramic composites have been summarized in Table 1, Figs. 10 and 11. The load vs. displacement plot, as shown in Fig. 12 has been used to determine Young’s Modulus using Oliver-Pharr method,35) which has been used for calculating indentation toughness using Eq. (2). It is clearly seen that Vickers hardness improves monotonically with increase in Ti content. There is a marginal increase in hardness with 5 wt.% Ti addition, whereas nearly 170% increase with 10 wt.% Ti addition, as compared to the base ceramic composite. Similarly, an increasing trend of indentation toughness with increasing Ti content has been observed, where highest
indentation toughness of 9 MPa m^{1/2} has been achieved in ZrB_{2}–SiC composite with 10 wt.% Ti addition. This corresponds to almost 230% increase with respect to the base ceramic composite without Ti additive. It is to be noted that although hardness does not appreciably improve in the composite with 5 wt.% Ti addition, but the fracture toughness is almost 1.5 times compared to the base composite. This is most probably due to the fact that 5 wt.% Ti addition is insufficient to obtain uniform distribution of sintering reaction products that increase the hardness of the composite as a whole. The steady improvement in the mechanical properties with Ti addition, agrees well with the fact that sinter density improves with Ti addition (refer Table 1). The increase in hardness values is attributed to finer microstructure obtained due to MS-SPS. It is interesting to note that with indentation load as high as 50 kg, the indent and cracks formed were symmetric as shown in Fig. 13(1), indicating superior mechanical properties. Figures 13(2) and 13(3) shows that the nature of crack propagation is transgranular, which is usually observed in ceramics. Evidently, the appearance of multiple crack deflections can be attributed to the homogeneous distribution of sintering reaction products in the ZrB_{2}, SiC matrix. Figure 13(4) shows the crack arrest at the interface of two grains of different compositions. It must also be noted here that sintering reaction products namely, ZrSi_{2}, TiSi_{2}, and TiC formed during sintering have a larger coefficient of thermal expansion (CTE) ([ZrSi_{2}] \approx 36 \times 10^{-6} K^{-1}, [TiC] \approx 7.7 \times 10^{-6} K^{-1}) than the matrix ([ZrB_{2}] \approx 6.2 \times 10^{-6} K^{-1})^{14,41,45} thereby resulting in the development of compressive residual stress in the matrix during cooling from the sintering temperature. It is believed that such compressive residual stress in the matrix contribute towards improving fracture toughness\(^{46,47}\) for the composites sintered via MS-SPS. This is in confirmation with the presence of crack deflections by different sintering reaction products. Besides, the finer microstructure obtained in the case of MS-SPS would minimize the possibility of spontaneous cracking at the grain interfaces due to residual strains generated during cooling.\(^{48}\) Furthermore, the homogeneity in the microstructural development achieved during MS-SPS, as compared to single stage SPS, would also impart superior fracture toughness to the composites sintered via this innovative sintering scheme.

The microstructure has also been examined to understand the increase in toughness with Ti additive and it has been found that the crack induced by applying 50 kg load, as shown in Fig. 14, has been deflected by different phases in the sintered ceramic and finally arrested by the light gray grains, which are rich in sintering reaction products. In order to further investigate this aspect, the composites were fractured under flexural loading and the fracture surfaces were examined. A representative secondary electron image of the fractured sample is shown in Fig. 15. The primary mode of fracture is observed to be transgranular with indication of intergranular fracture (Fig. 15(1)) as evidenced by the spalling of the tabular/elongated SiC grains and relatively smaller ZrB_{2} grains (Fig. 15(2)) on the fracture surface. A comparison of the mechanical properties of ZrB_{2}–SiC–Ti ceramics in the present study with previously developed ZrB_{2}–based composites is shown in Table 2. It can be observed that the ceramic developed in the present study, with 10 wt.% Ti addition, shows the most favourable combination of hardness (29.2 GPa) and indentation toughness (9 MPa m^{1/2}).

![Fig. 12. Typical load vs. displacement plot for Vickers hardness test performed on MS-SPSed ZrB_{2}–18 wt.% SiC–x wt.% Ti (x = 0, 5 & 10) samples.](image)

![Fig. 13. SEM image of 50 kg Vickers indent (1) and crack-microstructure interaction around the indents (2, 3 & 4) obtained on MS-SPS processed ZrB_{2}–18 wt.% SiC–10 wt.% Ti sample.](image)
3.6 Further work

We believe that the formation of various sintering reaction products primarily ZrSi2, TiSi2 and TiC have helped in enhancing hardness with increasing Ti addition. A detailed TEM investigation can reveal the finer scale microstructural features along with the identification of sintering reaction products and their interaction with the matrix, which can possibly help in understanding the toughening mechanism in the present case. Further investigations are required to optimize the sintering conditions to retain metallic Ti in order to achieve much better fracture toughness without sacrificing the essential hardness property for aerospace grade materials.

ZrB2-based UHTCs are the candidates for use in severe environments, where they are exposed to extreme heat flux and pressure. This necessitates the investigation of thermo-structural behaviour of ZrB2-based ceramics to evaluate their performance under extreme thermal and structural loads. Finite element based coupled thermo-structural analysis (CTSA) can provide the required insight to material researchers to tailor the ceramic processing in accordance with the structural requirements. In this perspective, we performed an evaluation of thermo-structural behaviour of hypersonic vehicle leading edge made of ZrB2-based UHTCs. The computational analysis methodology consists of Computational Fluid Dynamics (CFD) analysis to estimate the loads (pressure and heat flux), followed by load mapping to structural domain for performing CTSA. CFD analysis was carried using ANSYS FLUENT to calculate heat flux and pressure experienced by vehicle leading edge in hypersonic flow of Mach 7 at 30 km altitude. High fidelity structured mesh with second order elements was generated using commercial software HyperMesh. CTSA was carried out using commercial finite element package (ANSYS), which predicted maximum temperature of 1688°C at the end of 20 s and deformation of 1 mm at the nose of leading edge. Such high deformations can adversely affect the aerodynamics of the hypersonic vehicle. This necessitates the control of thermal expansion by minimizing CTE of ZrB2-based ceramics, which we suggest as an essential prop-

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Table 2. Comparison of mechanical properties and densities of ZrB2-based ceramics, from literature, illustrating the effect of different sinter additives on mechanical properties of ZrB2 (HP: hot pressing; PS: pressureless sintering; HIP: hot isostatic pressing; RHP: reactive hot pressing; *SENB: Single Edge Notch Bending)

| S. No. | Material composition (in wt.%) | Processing details | Relative density (% ρd) | Vickers hardness (Hv, GPa) | Indentation toughness (Kc, MPa m1/2) | Ref. |
|-------|------------------------------|-------------------|-------------------------|---------------------------|-------------------------------------|------|
| 1     | ZrB2                         | PS, 2150°C, 9 h   | 98                      | 14.5                      | 2.8                                 | [19] |
| 2     | ZrB2–30SiC                   | RHP, 1800°C      | 99                      | 27                        | 2.1                                 | [20] |
| 3     | ZrB2–20MoSi2                 | PS, 1850°C, 30 min | 99.1                    | 16.1                      | 2.3                                 | [21] |
| 4     | ZrB2–15TaSi2                 | HP, 1900°C       | 99                      | 17.8                      | 3.8                                 | [22] |
| 5     | ZrB2–18.5SiC–3.7Si3N4–1Al2O3–0.5Y2O3 | HP, 1760°C     | 98                      | 14.2                      | 4.6                                 | [23] |
| 6     | ZrB2–SiC                     | SPS, 1400°C, 30 MPa, 12 min | 98.3                    | 17.3                      | 5.3                                 | [50] |
| 7     | ZrB2–40ZrC–12SiC             | SPS, 1800°C, 20 MPa, 10 min | 99.5                    | 16.9                      | 5.9                                 | [51] |
| 8     | ZrB2–6Cu                     | SPS, 1500°C, 20 min | 95                      | 19.1                      | 7.4                                 | [13] |
| 9     | ZrB2–60SiC                   | SPS, 2100°C, 20 MPa, 3 min | 99                      | 26.8                      | 3.5                                 | [31] |
| 10    | ZrB2–6CNT                    | SPS, 1900°C, 70 MPa, 15 min | 99.3                    | 15.1                      | 3.5                                 | [32] |
| 11    | ZrB2–6GnPb                   | SPS, 1900°C, 70 MPa, 15 min | 96.9                    | 14                        | 2.8                                 | [33] |
| 12    | ZrB2–18SiC–5TiSi2            | SPS, 1600°C, 50 MPa, 10 min | 99.9                    | 20.3                      | 5.1                                 | [4]  |
| 13    | ZrB2–18SiC–2.5TiSi2          | MS-SPS, 1500°C, 30 MPa, 2 min | 99.9                    | 27                        | 4.7                                 | [4]  |
| 14    | ZrB2–10Mo                    | HP, 1950°C, 20 MPa, 60 min | 98.9                    | 17.5                      | 6.7                                 | [14] |
| 15    | ZrB2–40Nb                    | HP, 1800°C, 30 MPa, 60 min | 97                      | 14.6                      | 7.1                                 | [15] |
| 16    | ZrB2–18SiC                   | MS-SPS, 1600°C, 30 MPa, 5 min | 100                     | 17.5 ± 0.9                | 3.7 ± 0.7                           | Present work |
| 17    | ZrB2–18SiC–5Ti               | MS-SPS, 1600°C, 30 MPa, 5 min | 100                     | 20.4 ± 0.8                | 5.6 ± 0.5                           | Present work |
| 18    | ZrB2–18SiC–10Ti              | MS-SPS, 1600°C, 30 MPa, 5 min | 100                     | 29.2 ± 2.0                | 9.0 ± 0.9                           | Present work |
tery to be achieved by tailoring the processing of ZrB2–based ceramics.

In future, investigation of thermo-structural behaviour of ZrB2–based ceramics would be accomplished experimentally by exposing the ceramic composites to high enthalpy flow and comparing it with CTSAs.

4. Conclusions

The present work explores for the first time the use of Ti as sinter aid for ZrB2–SiC composites using innovative MS-SPS. The effect of Ti addition on mechanical properties and microstructural characterization for MS-SPSed ZrB2–SiC–Ti have been investigated and following are the major conclusions:

(a) An addition of Ti to ZrB2–18 wt. % SiC aids in achieving more than 99% ρ<sub>th</sub> under 30 MPa uniaxial pressure via multi stage sintering route at a maximum temperature of 1600°C. The densification rate of the ZrB2–based ceramics increases with an increasing amount of Ti sinter aid.

(b) Multiple sintering reaction products namely ZrSi2, TiSi2, TiC with minor traces of ZrC and TiO2 have formed during sintering with Ti addition. The inherent refractory nature of these products are believed to have contributed in enhancing the hardness and fracture toughness of the processed ceramic composites.

(c) Remarkable improvement in hardness is observed, such that ZrB2–18 wt. % SiC–10 wt. % Ti has hardness of 29.2 GPa and ZrB2–18 wt. % SiC–5 wt. % Ti has hardness of 20.4 GPa.

(d) An increase in Ti content resulted in improvement of Vickers hardness as well as indentation toughness, such that ZrB2–18 wt. % SiC–10 wt. % Ti possesses a good combination of hardness 29.2 GPa and indentation toughness 9 MPa m<sup>1/2</sup>.

(e) Microstructural analysis confirms the presence of SiC uniformly distributed in a matrix of ZrB2 along with traces of sintering reaction products. Average grain size of 2.4 ± 0.3 μm for ZrB2 with mean aspect ratio of 1.5 ± 0.2 and average grain size of 2.2 ± 0.6 μm with mean aspect ratio of 1.9 ± 0.2 for SiC have been measured.

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