# SPARK PLASMA SINTERING AND STRUCTURAL PROPERTIES OF ZrB$_2$ BASED CERAMICS: A REVIEW

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**Abstract.** Spark plasma sintering (SPS) is one of the most advanced techniques for consideration of highly refractory powders, and induced by applying uniaxial force and a pulsed direct current to execute quick sintering of powder or green compact. The direct pulse heating can generate very high heating and cooling rates, enhance diffusion mechanism and moreover, controlling the grain growth process. The basic phenomenal increase in the utilization of this technique in both industry and R&D sectors is to get the better structural properties in shorter processing time. In recent time, SPS technique is being increasingly used for consolidation of different materials like metals, cermet, ceramics, glass etc. ZrB$_2$ based ultra high temperature ceramics is one of the most promising materials in the current advanced structural ceramic applications. This review focuses, on one hand, the basic concept, definition of spark plasma sintering and on the other deals with the effect of various additives, such as carbides, nitrides and disilicides, on the densification behaviour and structural properties of zirconium diboride-based composites.

## 1. INTRODUCTION

In the field of structural ceramics and composites, namely, aerospace, armour, and other conventional applications like refractory crucible, thermal plant, atomic reactor, cutting tools, etc. performances are mainly dictated by high density and low defects and porosity, homogeneous microstructure, uniform distribution of the secondary phase in the matrix [1,2]. In recent research, a new promising direction has been explored within the family of transition metal based borides, carbides, and nitrides called ultra-high temperature ceramics (viz., ZrB$_2$, TaB$_2$, TiB$_2$, ZrC, WC, ZrN, TaN, HfN, etc.) have unique combinations of mechanical, tribological, and physical properties at very high temperature, including high melting point (> 3000 °C), high hardness, fracture toughness, and bending strength, high thermal and electrical conductivities, chemical inertness against corrosive atmosphere and great thermal shock resistance [3-5]. In this regard, UHTCs are considered the most promising candidate materials for the fabrication of thermal protection systems components (leading edge, nozzle, jet-vane) for hypersonic flights and atmospheric re-entry vehicles that will be able to withstand harsh flow conditions. Other important conventional applications of this class of materials include solar absorber, molten metal crucibles, electric discharge machining electrodes, plasma electrode, and microelectronics [4,5].

Among UHTC family, zirconium diboride has excellent combination of good mechanical properties like hardness (>22 GPa), thermal conductivity

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(60-80 W/m K$^{-1}$), electrical conductivity (1.0×10$^7$ S/m), high chemical inertness and oxidation resistance in adverse atmosphere, and lowest theoretical density (6.09 g/cc) [4,5]. Moreover, its low cost makes it a promising material for advance aerospace and thermal power applications [6]. Zirconium diboride is covalent in nature and has low self-diffusion rate; the presence of surface oxide layers (ZrO$_2$, TiO$_2$, B$_2$O$_3$) causes additional difficulties in the sintering of the powders [7-9]. It has hexagonal P6/mmm symmetry and the structure is formed by alternation of Zr and B planes [10]. The Zr planes are arranged in hexagonal close-packed structure and B planes are formed in sp$^2$ hybridization. Each Zr atom is surrounded by six in plane Zr atoms and 12 out of plane B atoms [11-12]. The ZrB$_2$ structure consists of Zr-Zr metallic bonds, B-B covalent bonds, and Zr-B both covalent and ionic bonds [13]. The presence of free valence electron in Zr-Zr metallic bond generates high electrical and thermal conductivity and, on the other hand, B-B covalent bond contributes to the stiffness of the crystal as well as hardness, fracture strength and chemical inertness of the ZrB$_2$ material. Moreover, strong Zr-B bond contributes high melting temperature of ZrB$_2$ material [4].

For making high density and low defect sample, precursor ZrB$_2$ powder can be hot pressed (HP) or hot isostatic pressed (HIP) at high temperature. But these sintering techniques take longer time, consume high electrical energy, need large foundry and critical encapsulation technologies. Moreover, longer heating and soaking time during sintering processes generate coarse microstructure in the sintered samples that affect their structural properties. Therefore, major research largely focused on using various other sintering techniques i.e. spark plasma sintering (SPS), microwave sintering, laser sintering, etc. to attain maximum densification and to improve the structural properties of borides. This review is divided into two parts. The first part focuses on basic concept, definition of spark plasma sintering and the second part deals with the effect of second phase additives, such as different carbides, nitrides, and disilicides, on the densification behaviour and structural properties of zirconium diborides based composites.

## 2. BASIC OF SPARK PLASMA SINTERING TECHNIQUE

Spark plasma sintering (SPS) or field assisted sintering technique (FAST) is a most advanced processing technique that allows compaction of bulk material from powder using direct electrical current under fast heating rate (500 °C/min or faster depending upon the sample size and its electrical conductivity) [14]. SPS makes use of a unidirectional alternating current (ac) or direct current (dc) ultimately superimposed to a direct current with different electric current waveform and the dc pulse is applied repeatedly from the beginning to the end of the heating schedule. Recently, this SPS technique has been referred to as different forms like pulsed electric current sintering (PECS), plasma activated sintering (PAS), and current activated pressure activated densification. However, the main classifications of SPS systems are based on the capacity, discharge time, electric current density, and waveform. The sinterability of the precursor powder in SPS technique is accelerated due to low-voltage (~10 V) and high DC current (20000 A or higher) that can be directly applied into the powder or green compact though high density graphite mould and the sintering activity is automatically increased at the points of contact of the particles (generation of plasma, Joule heating, electro migration, electroplasticity, etc.) [15].

(i). Generation of plasma: It was reported by many researchers that dc pluses generated sparks and plasma between the particles contacts [16,17]. Moreover, ionization and also the cleaning of surface impurities and oxide layers at the particle surface occurred due to spark discharging. But there was no convincing experimental evidence.

(ii). Joule heating: This effect happens at the particles conducting surface by localized evaporation and cleaning of the powder surfaces [18].

(iii). Pulse current: The ON-OFF pattern of dc pulse generates sparking, spark impact pressure, high speed ion migration, efficient generation of pulse voltage and current, diffusion by electrical field and finally heat transfer from high temperature to low temperature of the sample. The later is active during pulse OFF time [14]. This direct way of sintering helps the technique of very high heating and cooling rates, enhancing densification by suppressing grain growth. The overall heat flux concentrates in two parts namely, localized sparking and massive heating. The former heating occurs on the particles interfaces followed by physical bonding and the latter promotes plastic deformation during sintering. The reported advantages of SPS techniques are: (i) single step quick sintering process, (ii) low power consumption w.r.t hot press, hot isostatic press, (iii) particle surface cleaning (metal and oxide impurities) during electric discharge, (iv) accurate and selective control of sintering, density and

porosity, (v) retaining initial grain size of the powder, (vi) near net shaped fabrication, (vii) consolidation of amorphous, nanopaticles and reactive compounds, (viii) high production rate. But the main drawbacks of this technique are, on difficulties of fabrication of bigger size sample due to inhomogeneous temperature gradient of the sample and also require adequate electrical conductivity of the ceramic powder to achieve uniform temperature distribution.

The SPS technology was initially stimulated by the metal and current industries in early 1960. But very few successful technologies and papers were reported elsewhere before 1990 [19]. The reasons beside the discontinuous progress of the SPS technology were the lack of fundamental understanding of the basic of SPS science and the requirement of huge and heavy foundation that might be initially hindered by the industry management. More than 3000 papers were published in last four decades on SPS and the publications started to grow abruptly since the two decades [20,21]. In the early 1990s, Sumitomo Coal Mining Co. Ltd., Japan first commercialised the most advanced semi-automatic SPS furnace (Dr. Sinter series) with dc pulse generator [22,23]. This process allows operators without previous experience to fabricate high-quality sintered products with minimal cost. In December 1998, SPS production systems of Fuji Electronic Indus-trial Co. Ltd., Japan tied up with Sumitomo Heavy Industries, Ltd., Japan and included the standard Dr. Sinter Lab series for use in research and education. Later other companies like Thermal Technology LCC, USA, Dr. Fritsch Sondermaschinen GmbH, Germany and FCT Systeme GmbH, Germany took part for fabrication of most advanced SPS furnace with bigger sizes (up to 300 mm diameter); see Table 1. This production capacity of a SPS unit is not only ruled by the high heating rate and shorter soaking but also by a faster cooling set-up which permits quick cooling into the sintering chamber and zone.

## 3. SPARK PLASMA SINTERING OF ZrB₂ SYSTEM

Spark plasma sintering (SPS) is a well known novel technique for processing difficult-to-sinter materials like $ZrB_2$. Many researchers are using SPS techniques for making both reaction synthesis and densification in one single processing step, known as reactive SPS (RSPS), using suitable reactants as starting materials [24,25]. As far as the spark plasma sintering and optimum densification are concerned, significant researches are directed on towards optimizing processing parameters and addition of different promoters or second phases [26,27]. For low

**Table 1.** Specifications of different SPS furnace models.

| Company | Model | Maximum voltage/ current/powder | Applied load (Max.) | Max. specimen dia. ($\varnothing$, mm) |
|---|---|---|---|---|
| Fuji Electronic | SPS-3.20MK-IV | 8000 A | 200 kN | - |
| Industrial Co. | SPS-5.40MK-IV | 8000 A | 500 kN | - |
| Ltd., Japan | SPS-5.40SMK-IV | 8000 A | 500 kN | - |
| (Dr. Sinter) | SPS-7.40MK-V | 10000 A | 1000 kN | - |
| | SPS-9.40MK-VII | 20000 A | 3000 kN | - |
| Thermal | SPS 10-4 | 4000 A | 10 tons | - |
| Tech. Inc., | SPS 25-10 | 10000 A | 25 tons | - |
| USA | SPS100-30 | 30000 A | 100 tons | - |
| Dr. Fritsch | DSP 507 | 79 kVA | 259 kN | 165 |
| Sondermaschinen | DSP 510 | 110 kVA | 368 kN | 180 |
| GmbH, Germany | DSP 515 | 170 kVA | 603 kN | 180 |
| | DSP 517 | 205 kVA | 603 kN | 350 |
| FCT Systeme | HP D 10 | 7.2 V, 5500A | 100 kN | 50 |
| GmbH, Germany | HP D 25 | 8 V, 8000A | 250 kN | 80 |
| | HP D 60 | 8 V, 16000A | 600 kN | 120 |
| | HP D 125 | 8 V, 24000A | 1250 kN | 150 |
| | HP D 250 | 8/16 V, 24000/ 48000A | 250 kN | 300 |
| | H-HP D 25 | 60-80 kW | 250 kN | 100 |
| | H-HP D 60 | 120 kW | 600 kN | 150 |
| | H-HP D 250 | 300 kW | 2500 kN | 300 |

temperature sintering of ZrB$_2$ ceramic, there are mainly two different ways, namely by using different carbides like SiC, ZrC, Zr$_2$Al$_4$C$_5$, etc. to remove surface oxide layers or by using low melting point additives like TiSi$_2$, MoSi$_2$ etc. for making liquid phase at the interfaces of the ZrB$_2$ grain boundaries [28-72]. Table 2 summarizes the work related to spark plasma sintering and structural properties of ZrB$_2$ monolithic and its composites. I. Akin et al. sin-

tered ZrB$_2$-SiC (20-60 mass %) composites by SPS technique in the range of 2000-2100 °C for 3 min and achieved a maximum relative density of more than 99% [28]. Morphological change from equiaxed to elongated α-SiC grains was observed at higher sintering temperatures and the mechanical properties of ZrB$_2$-SiC composites increased with increasing sintering temperature and SiC content up to 60 mass %. The highest hardness and fracture tough-

**Table 2.** Spark plasma sintering and structural properties of ZrB$_2$ based composites.

| Composition | Sintering Condition | Density | Structural Properties | Ref |
|---|---|---|---|---|
| i. ZrB$_2$-SiC (60 wt.%) <br> ii. ZrB$_2$-SiC (50 wt.%) | 2100 °C/3 min, 10 MPa, Vacuum, $T_{on}$- 60 ms, $T_{off}$-10 ms | R.D: 99% | i. $H_v$: 26.8 GPa <br> ii. $K_{IC}$: 4.1 MPa·m$^{1/2}$ <br> σ: 380 MPa | 28 |
| ZrB$_2$-ZrO$_2$(f) (30 vol.%) | 1600-1800 °C/10 min, 25 MPa | R.D: 96.5-99.2% | $K_{IC}$: 4.4-6.2 MPa·m$^{1/2}$ <br> $σ_{fs}$: 523-667 MPa | 29 |
| ZrB$_2$-Al$_3$BC$_3$ (15 wt.%) | 1700 °C/10 min, 40 MPa, Vacuum, $T_{on}$- 12 ms, $T_{off}$-2 ms | R.D: 99.5% | $K_{IC}$: 6.17 MPa·m$^{1/2}$ <br> $σ_{fs}$: 529 MPa | 30 |
| ZrB$_2$-SiC (10-30 vol.%) -TaSi$_2$ (10-20 vol.%) | (i). 1600 °C/10 min, 30 MPa, Vacuum, $T_{on}$- 12 ms, $T_{off}$-2 ms | (i). ρ:5.07-5.59 g/cc | (i). $H_v$:19.8-22.4 GPa <br> $K_{IC}$: 4.02-4.79 MPa·m$^{1/2}$ <br> $E$:437.6-459.3 GPa | 31 |
| | (ii). 1800 °C/10 min, 30 MPa,Vacuum, $T_{on}$- 12 ms, $T_{off}$-2 ms | (ii). ρ:5.11-5.64 g/cc | (ii). $H_v$:19.4-21.2 GPa <br> $K_{IC}$: 4.03-4.89 MPa·m$^{1/2}$ <br> $E$:452.9-463.9 GPa | |
| ZrB$_2$ (70 mol.%)- ZrC (15 mol.%)-SiC (15 mol.%) | 1950 °C/2 min, 50 MPa, Argon | ρ:5.85 g/cc | $H$: 21.5±1.3 GPa <br> $K_{IC}$: 6.0±0.5 MPa·m$^{1/2}$ <br> $E$: 517 GPa <br> $G$: 225 GPa ν: 0.16 | 32 |
| ZrB$_2$-MoSi$_2$ (9 wt.%) | 1700 °C/5 min, 100 MPa | R.D: 100% | $H_v$: 18.2±0.7 GPa <br> $K_{IC}$: 3.3±0.5 MPa·m$^{1/2}$ | 33 |
| ZrB$_2$-GNP (6 vol.%) | 1900 °C/15 min, 70 MPa, Argon | R.D: 96.9% | $H_v$: 14.0±0.6 GPa <br> $K_{IC}$: 2.77±0.06 MPa·m$^{1/2}$ <br> $σ_{fs}$: 316±85 MPa | 34 |
| ZrB$_2$-Cu (6 wt.%) | 1500 °C/15 min, Vacuum | R.D: 94.8% | $H_v$: 19.1 GPa <br> $K_{IC}$: 7.4 MPa·m$^{1/2}$ | 35 |
| ZrB$_2$-Zr$_2$Al$_4$C$_5$ (10-40 vol.%) | 1800 °C/3 min, 20 MPa, Vacuum | ρ:5.15-5.80 g/cc | $H_v$: 13.4-15.3 GPa <br> $K_{IC}$: 2.55-4.20 MPa·m$^{1/2}$ <br> $E$: 362-452 GPa | 36 |
| ZrB$_2$-SiC (20 vol.%) | 1900 °C/5 min, 50 MPa, Vacuum | ρ:5.40-5.62 g/cc | $H_v$: 19.2-20.2 GPa <br> $K_{IC}$: 3.5-4.7 MPa·m$^{1/2}$ | 37 |
| ZrB$_2$-SiC$_f$ (20 vol.%)- Si$_3$N$_4$ (5 vol.%) | 1500 °C/5 min, 50 MPa, Argon | ρ:4.7 g/cc | $K_{IC}$: 5.53±0.37 MPa·m$^{1/2}$ <br> $σ_{fs4pt}$: 370±20 MPa (RT) <br> $σ_{fs4pt}$:447±23 MPa (1200) | 38 |
| ZrB$_2$-ZrH$_2$ (4.94-19.17 wt.%) | 1900 °C/5 min, 50 MPa, Vacuum, $T_{on}$- 10 ms, $T_{off}$-3 ms | ρ:6.09-6.25 g/cc | $H_v$: 15.1-17.1 GPa <br> $K_{IC}$: 4.3-5.0 MPa·m$^{1/2}$ <br> $E$: 469-512 GPa <br> $σ_{fs3pt}$: 852-1382 MPa | 39 |

| Material | Processing | R.D. | Properties | Ref. |
|---|---|---|---|---|
| $ZrB_2$ monolithic | 2100 °C/15 min, 35 MPa, Argon, $T_{on}$- 10-100 ms, $T_{off}$-1-100 ms | R.D: 97.41-98.65% | $H_v$: 15.32-16.64 GPa<br>$K_{IC}$: 2.75-4.69 MPa·m$^{1/2}$ | 40 |
| $ZrB_2$-$MoSi_2$ (15 vol.%) | 1750 °C/8 min, 30 MPa | R.D: 98% | $H_v$: 16.20 GPa<br>$K_{IC}$: 3.50 MPa·m$^{1/2}$ | 41 |
| $ZrB_2$-SiC | 1400 °C/3-12 min, 20-65 MPa | R.D: 96.3-98.3% | $H_v$: 11.70-18.6 GPa<br>$K_{IC}$: 3.60-5.30 MPa·m$^{1/2}$ | 42 |
| (i). $ZrB_2$-$MoSi_2$ (15 vol.%) | (i).1750 °C/7 min, 30 MPa, Vacuum | (i). R.D: 98.3% | (i). $H_v$: 16.20±0.5 GPa<br>$K_{IC}$: 4.4±0.6 MPa·m$^{1/2}$<br>$\sigma_{fs}$: 643±97 MPa<br>$E$: 479 GPa | 43 |
| (ii). $ZrB_2$ (60 vol.%)-ZrC (30 vol.%)-SiC (10 vol.%) | (ii). 2100 °C/2 min, 30 MPa, Vacuum | (ii). R.D: 99.0% | (ii). $H_v$: 18.80±0.5 GPa<br>$K_{IC}$: 3.5±0.2 MPa·m$^{1/2}$<br>$\sigma_{fs}$: 723±136 MPa<br>$E$: 474 GPa | |
| (i). $ZrB_2$-SiC (25 vol.%) | 1800 °C/30 min, 20 MPa | (i). R.D: 99.6% | (i). $H_v$: 16.70± 0.4 GPa<br>$K_{IC}$: 5.0±0.3 MPa·m$^{1/2}$ | 44 |
| (ii). $ZrB_2$-ZrC (40 vol.%) -SiC (12 vol.%) | | (ii). R.D: 98.7% | (ii). $H_v$: 16.90±0.2 GPa<br>$K_{IC}$: 5.9±0.5 MPa·m$^{1/2}$ | |
| (i). $ZrB_2$-SiC (20 vol.%) | 1550 °C/ 8 min, 40 MPa | (i). R.D: 98.62% | (i). $H_v$: 16.18±0.63 GPa<br>$K_{IC}$: 3.73±0.11 MPa·m$^{1/2}$<br>$E$: 440±14 GPa | 45 |
| (ii). $ZrB_2$-SiC (20 vol.%)-BNNT-BNNP (0.5 wt.%) | | (ii). R.D: 98.71% | (ii). $H_v$: 15.38±0.85 GPa<br>$K_{IC}$: 4.33±0.26 MPa·m$^{1/2}$<br>$E$: 445±17 GPa | |
| (iii). $ZrB_2$-SiC (20 vol.%)-BNNT-BNNP (1 wt.%) | | (iii). R.D: 98.75% | (iii). $H_v$: 16.50±1.38 GPa<br>$K_{IC}$: 4.64±0.36 MPa·m$^{1/2}$<br>$E$: 441±24 GPa | |
| $ZrB_2$- SiC (20 vol.%) -$Yb_2O_3$(5 vol.%) | 1900 °C/ 4 min, 30 MPa, Vacuum | - | $H_v$: 17.30±0.30 GPa<br>$K_{IC}$: 3.51±0.01 MPa·m$^{1/2}$<br>$\sigma_{fs}$: 687±30 MPa | 46 |
| $ZrB_2$- SiC (15-30 vol.%) | 1375 °C/5 min, 25 MPa, Vacuum | R.D: 93.1-94.2% | $H_v$: 10.50-11.10 GPa<br>$s_{fs}$: 335.50- 391.60 MPa<br>Mass Ablation rate:<br>0.115- 0.261 mg/cm$^2$.s | 47 |
| (Zr, Hf)$B_2$-SiC | 1600 °C/ 10 min, 40 MPa, Vacuum | R.D: 98.30% | $H_v$: 17 GPa<br>$K_{IC}$: 5.36 MPa·m$^{1/2}$<br>$\sigma_{fs}$: 641MPa,<br>$E$: 468 GPa | 48 |
| $ZrB_2$- SiC | 1800 °C/ 5 min, 40 MPa | R.D: 97.9% | $\sigma_{fs}$:310 MPa | 49 |
| $ZrB_2$-$MoSi_2$ | 1700 °C/ 5 min, 70 MPa | R.D: >99% | $H_v$: 15.5 GPa (nontextured)<br>: 16.4 GPa (c-axis)<br>: 15.6 GPa (a, b -axis)<br>$\sigma_{fs}$: 576.3 MPa (nontextured)<br>: 557.5 MPa (c-axis)<br>: 315.4 (a, b -axis)<br>$E$: 414.7 GPa (nontextured)<br>: 405.1 GPa (c-axis)<br>: 418.3 GPa (a, b -axis) | 50 |

| | | | | |
|---|---|---|---|---|
| ZrB$_2$ (95 wt.%)-SiC (5 wt.%)-ZrO$_2$(f) (0-20 wt.%) | 1700 °C/ 5 min, 50 MPa | R.D: 92.98-94.34% | $H_v$: 9.66-11.87 GPa<br>$K_{IC}$: 5.05-6.56 MPa·m$^{1/2}$<br>$\sigma_{fs}$: 293-580 MPa | 51 |
| ZrB$_2$-SiC (20 vol.%)-La$_2$O$_3$ (2 wt.%) | 1950 °C/ 3-6 min, 50 MPa, Vacuum | R.D: 99.1-99.6% | $H_v$: 19.3-21.1 GPa<br>$K_{IC}$: 5.2-6.4 MPa·m$^{1/2}$<br>$\sigma_{fs}$: 600-700 MPa (RT)<br>: 358-400 MPa (1400 °C) | 52 |
| ZrB$_2$-Cu (15 wt.%) | 1650 °C/5 min | - | $H_v$: 10.16 GPa<br>$K_{IC}$: 7.0 MPa·m$^{1/2}$<br>$\sigma_{fs}$: 593.33 MPa | 53 |
| ZrB$_2$-YAG | 1700 °C/ 4 min, 20 MPa | - | $K_{IC}$: 3.76 MPa·m$^{1/2}$<br>$E$: 430 GPa | 54 |
| ZrB$_2$ (48 vol.%)-SiC (24 vol.%)-BN (28 vol.%) | 1850 °C/ 5 min, 4 MPa | $\rho$:4.17-4.19 g/cc | $H_v$: 9.38-9.67 GPa<br>$E$: 250.2-253.1 GPa<br>$G$: 107.9-108.3 GPa<br>$v$: 0.158-0.164<br>$\sigma_{fs}$: 393.5-472.6 MPa | 55 |
| ZrB$_2$-Al$_3$BC$_3$ (5 wt.%) | 1700 °C, 60 MPa | R.D: 99.9% | $H_v$: 20.04 GPa<br>$K_{IC}$: 3.37 MPa·m$^{1/2}$ | 56 |
| ZrB$_2$ (40-75 vol.%) - SiC (20-25 vol.%) - Zr$_2$Al$_4$C$_5$ (0-40 vol.%) | 1800 °C/ 3 min, 20 MPa | $\rho$:4.79-5.20 g/cc | $H_v$: ~13.2-18.9 GPa<br>$K_{IC}$: ~3.8-5.3 MPa·m$^{1/2}$<br>$E$: 462- 382 GPa | 57 |
| (i). ZrB$_2$-SiC (10-40 vol.%) | 1900 °C/15 min, 70 MPa, Argon | (i). R.D: 99.1-99.7% | (i) $H_v$: 19.38-22.71 GPa<br>$K_{IC}$: 1.92-2.66 MPa·m$^{1/2}$<br>$\sigma_{fs}$: 301-553 MPa | 58 |
| (ii). ZrB$_2$-CNT (2-6 vol.%) | | (ii).R.D: 95.3 -99.3% | (ii). $H_v$: 14.17-16.39 GPa<br>$K_{IC}$: 1.53-3.53 MPa·m$^{1/2}$<br>$\sigma_{fs}$: 151-315 MPa | |
| ZrB$_2$-SiC (18 wt.%)-TiSi$_2$ (0-5 wt.%) | 1600 °C/ 10 min, 50 MPa, Vacuum | R.D: 87.8-100% | $H_v$: 17.1-20.3 GPa<br>$K_{IC}$: 3.17-5.07 MPa·m$^{1/2}$<br>$\sigma_{fs}$: 373-497 MPa | 59 |
| ZrB$_2$ (50-60 vol.%)-ZrC (40-20 vol.%)-SiC (10-20 vol.%) | 1750 °C/ 5 min, 40 MPa, Vacuum | R.D: 99.24-99.65% | $H_v$: 17.1-20.3 GPa<br>$K_{IC}$: 4.58-5.46 MPa·m$^{1/2}$ | 60 |
| ZrB$_2$-SiC (5-30 vol.%)-TaSi$_2$ (5 vol.%) | 1800 °C/ 5 min, 30 MPa, Vacuum | - | $H_v$: 16.9-20.2 GPa<br>$K_{IC}$: 3.70-4.44 MPa·m$^{1/2}$<br>$E$: 453.2-464.8 GPa | 61 |
| ZrB$_2$-Si$_3$N$_4$ (5 vol.%)-SiC$_w$ (10-20 vol.%)/ SiC$_f$ (-20 vol.%) | 1500 °C/ 3 min, 50 MPa, Vacuum | $\rho$:5.10-5.85 g/cc | $K_{IC}$: 3.75-5.73 MPa·m$^{1/2}$<br>$E$: 378-424 GPa<br>$\sigma_{fs}$: 373-769 MPa (RT)<br>$\sigma_{fs}$:393-447 MPa (1200 °C) | 62 |
| ZrB$_2$-MoSi$_2$ (0-9 vol.%) | 1700-1900 °C/ 3-5 min, 65 MPa, Vacuum | R.D: 98-100% | $H_v$: 18.2±0.7 GPa<br>$K_{IC}$: 4.0±0.6 MPa·m$^{1/2}$ | 63 |
| ZrB$_2$-ZrC (40 vol.%)-SiC (12 vol.%) | 1800 °C/3 min, 20 MPa | R.D: 90.6±1.4% | $H_v$: 16.9±0.2 GPa<br>$K_{IC}$: 5.9±0.5 MPa·m$^{1/2}$ | 64 |
| ZrB$_2$ (85-100 vol.%)-SiC$_w$ (5-15 vol.%)-AlN (0-5 vol.%)-Si$_3$N$_4$ (3-5 vol.%) | 1550 °C | R.D: 97-100% | $K_{IC}$: 5.46 -8.50 MPa·m$^{1/2}$<br>$\sigma_{fs}$: 416-566 MPa | 65 |
| ZrB$_2$-ZrC (Zr/B/C=2/2/1) (molar ratio) | 1800 °C/ 5-10 min, 40 MPa,Vacuum | R.D: 96.9-98.5% | $H_v$: 13.7-17.8 GPa<br>$K_{IC}$: 3.8-4.5 MPa·m$^{1/2}$ | 66 |

| | | | | |
|---|---|---|---|---|
| $ZrB_2$ (58 mol.%)-$ZrC$ (42 mol.%)-La (1-5 wt.%) | 1800 °C/ 5 min, 50 MPa, Vacuum | R.D: 98.5% | $K_{IC}$: 2.62 -2.56 MPa·m$^{1/2}$ | 67 |
| $(Zr,Ti)B_2$-$(Zr,Ti)N$ 30 MPa, Vacuum | 1600-1900 °C/ 5 min, | ρ:5.18-5.77 g/cc | $H_v$: 16.7-19.2 GPa $K_{IC}$: 2.42-4.76 MPa·m$^{1/2}$ $E$: 350-474 GPa $G$: 151-206 GPa ν: 0.14-0.17 | 68 |
| $ZrB_2$ (60-100 wt.%)-SiC (0-20 wt.%)-ZrC (0-38 wt.%) | 1800 °C/ 4 min | R.D: 90.5-99.7% | $H_r$: 88.32-92.24 $σ_{fs}$: 32.80-302.29 MPa | 69 |
| $ZrB_2$-ZrC [Zr/B/C = 3:2:2-6:10:1] (molar ratio) | 1800 °C/ 5 min, 40 MPa, Vacuum | R.D: 98% | $H_v$: 17.8 GPa $K_{IC}$: 3.8 MPa·m$^{1/2}$ | 70 |
| $ZrB_2$-$SiC_p$ (w/w 80:20) | 1900-2100 °C/ 15 min, 50 MPa, $t_{on}$= 50 ms, $t_{off}$= 5 ms | R.D: 91.91-93.04% | $H_v$: 16.22 GPa $K_{IC}$: 3.69 MPa·m$^{1/2}$ | 71 |
| $ZrB_2$-SiC (5 wt.%) | 1600-1700 °C/ 10 min, 15 kN, Vacuum | R.D: 91.91-97.70% | $K_{IC}$: 5.018-8.205 MPa·m$^{1/2}$ | 72 |

$T_{on}$= Pulse on time, $T_{off}$= Pulse off time, ρ= Bulk density, R.D= Relative density, $H_v$= Vicker's hardness, $H_r$= Rockwell hardness, $K_{IC}$= Fracture toughness, σ= Tensile strength, $σ_{fs}$=flexural strength, $E$= Young modulus, $G$= Shear modulus, ν= Poisson ratio, GNP= Graphene nanoplates, BNNT= Boron nitride nanotube, BNNP= Boron nitride nanoplatelets.

ness values were 26.8 GPa ($ZrB_2$-SiC (60 wt.%)) and 4.1 MPa·m$^{1/2}$ ($ZrB_2$- SiC (50 wt.%)), respectively. J. Lin et al. reported that high flexural strength of 667±48 MPa and fracture toughness of 6.2±0.6 MPa·m$^{1/2}$ were achieved for the $ZrB_2$-$ZrO_2$(f) (30 vol.%) ceramics spark plasma sintered at 1750 °C for 10 min soaking, with a holding pressure of 25 MPa [29]. High density and small grain size were the main issue to improve the mechanical properties of the $ZrO_2$ fibre reinforced $ZrB_2$ composite. H. Wang et al. showed that both fracture toughness and flexural strength of spark plasma sintered $ZrB_2$ composites at room temperature increased with the addition of $Al_3BC_3$ as sintering additive, which respectively achieved a maximum of 6.17 MPa·m$^{1/2}$ and 529 MPa at 15 wt.% $Al_3BC_3$ content [30]. C. Hu el al. formed a core-shell structure with the core being formed by $ZrB_2$ and the shell containing both Ta and Zr as $(Zr,Ta)B_2$ at 1600 °C [31]. It was observed that the formation of fine microstructure and introduction of Ta atoms into $ZrB_2$ by forming $(Zr,Ta)B_2$ solid solution would enhanced the hardness (up to 22.4 GPa), fracture toughness (up to 4.79 MPa·m$^{1/2}$) and Young's modulus (up to 459.3 GPa) values. When the sintering temperature was increased up to 1800 °C, only $(Zr,Ta)B_2$ solid solution and SiC phases observed in the samples and the core-shell structure disappeared. S. Q. Gao et al. prepared $ZrB_2$-ZrC-SiC composites with equiaxed $ZrB_2$, ZrC,

and SiC grains by SPS at 1950 °C and the results indicated that the shear modulus, Young's modulus, hardness and fracture toughness values were in the range of 180-225 GPa, 435-517 GPa, 18.8-21.5 GPa, and 4.6-6.1 MPa·m$^{1/2}$, respectively [32]. D. Sciti et al. consolidated $ZrB_2$ based composites containing 1, 3 and 9 vol.% $MoSi_2$ as a liquid phase by spark plasma sintering at different temperatures (1700 to 1950 °C) and it was found that the hardness and fracture toughness values were in the range of 17-22 GPa and of 2.6-4.0 MPa·m$^{1/2}$, respectively [33]. G. B. Yadhukulakrishnan et al. sintered $ZrB_2$ reinforced with 2-6 vol.% graphene nanoplates (GNPs) by SPS at 1900 °C and the composites reinforced with 6 vol.% GNPs exhibited highest flexural strength (316 MPa) [34]. However, the hardness of all the composites (2-6 vol.% GNPs) was varied in the range of 13.5-15.9 GPa without any specific trend with increasing GNP content. T. Venkateswaran et al. reported that a core-rim structure of $ZrB_2$/Cu (6 wt.%) cermet formed with the dissolution of Zr in Cu melt and achieved high hardness of 19.1 GPa and fracture toughness of 7.4 MPa·m$^{1/2}$, respectively [35]. Moreover, grain shape also changed from equiaxed to more rounded due to the dissolution-reprecipitation phenomenon of inherence in liquid phase sintering. Q. Guo et al. consolidated $ZrB_2$/$Zr_2Al_4C_5$ composite by spark plasma sintering technique at 1800 °C and it was

found that ZrB$_2$ composite with 40 vol.% of Zr$_2$Al$_4$C$_5$ showed the optimized microstructure and excellent fracture toughness value of 4.25 MPa·m$^{1/2}$, which was about 70% higher than that of the monolithic ZrB$_2$ [36]. Higher fracture toughness was mainly attributed to the in situ formed Zr$_2$Al$_4$C$_5$ phases and homogeneous microstructure of ZrB$_2$. S. Ran et al. reported that ZrB$_2$-20 vol.% SiC powder in situ synthesized and densified with a powder mixture containing ZrH$_2$, B, SiC and B$_4$C by the SPS technique and the structural properties of the composite like 3-point flexural strength, fracture toughness and Vickers' hardness were in the range of 901-937 MPa, 3.8-4.7 MPa·m$^{1/2}$, and 19.7-21.3 GPa, respectively [37]. D. Sciti et al. incorporated SiC chopped fibers (20 vol.%) for improving the fracture toughness of monolithic ZrB$_2$ ceramics from 3-4 MPa·m$^{1/2}$ (for unreinforced materials) to 5.7-6.2 MPa·m$^{1/2}$ [38]. S. Ran et al. sintered ZrB$_2$ (80 vol.%)-ZrB (20 vol.%) composite derived from a 9.8 wt.% ZrH$_2$ w.r.t ZrB$_2$ powder exhibited excellent flexural strength, Vickers hardness and fracture toughness of 1382 MPa, 17.1 GPa and 5.0 MPa·m$^{1/2}$, respectively [39]. The addition of ZrH$_2$ with ZrB$_2$ reacted and converted the B$_2$O$_3$ oxide layer on the ZrB$_2$ starting powder into ZrO$_2$ and ZrB$_2$, eliminating B$_2$O$_3$ evaporation. S. Chakraborty et al. reported the effect of pulse on-off patterns on densification and mechanical properties of pure ZrB$_2$ in details and the Vickers' hardness, fracture toughness at 1 kgf load and wear volume and wear rate at 10 N load of 2100°C temperature spark plasma sintered ZrB$_2$ samples at $t_{on}$ = 50 ms and $t_{off}$ = 5 ms pulse conditions achieved up to 16.64 GPa, 4.69 MPa·m$^{1/2}$, 4.05X10$^4$ μm$^3$, and 1.01X10$^{-3}$ mm$^3$/N m, respectively [40]. A. Balbo et al. consolidated ZrB$_2$-15 vol.% MoSi$_2$ composite by spark plasma sintering at 1750 °C and the hardness, fracture toughness values of the composite achieved up to 16.20 GPa, 3.50 MPa·m$^{1/2}$, respectively [41]. Y. Zhao et al. fabricated ZrB$_2$-SiC composites by spark plasma sintering reactive synthesis (SPS-RS) method and the fracture toughness values increased from 4.3±0.2 MPa·m$^{1/2}$ to 5.3±0.3 MPa·m$^{1/2}$ when the holding time prolonged from 9 min to 12 min at 1400 °C, whereas, hardness was not affected much by the processing condition, when the density was above 96.3% [42]. Furthermore, the hardness value decreased from 17.3±0.3 to 18.6±0.5 GPa when the holding time increased from 9 min to 12 min as a result of the grain growth of ZrB$_2$ and SiC. A. Bellosi et al. sintered both ZrB$_2$-15 vol.% MoSi$_2$ and ZrB$_2$ (60 vol.%)-ZrC (30 vol.%)-SiC (10 vol.%) composites by spark plasma sintering at two different temperatures i.e 1750 °C and 2100 °C, re-

spectively, and achieved highest hardness, fracture toughness, flexural strength and Young modulus for ZrB$_2$-15 vol.% MoSi$_2$ and ZrB$_2$ (60 vol.%)-ZrC (30 vol.%)-SiC (10 vol.%) composites were 16.20±0.5 GPa, 4.4±0.6 MPa·m$^{1/2}$, 643±97 MPa, 479 GPa, and 18.80±0.5 GPa, 3.5± 0.2 MPa·m$^{1/2}$, 723±136 MPa, 474 GPa, respectively [43]. R. Licheri et al. first synthesized ZrB$_2$-SiC (25 vol.%) and ZrB$_2$-ZrC (40 vol.%)-SiC (12 vol.%) batch powders by SHS process and then consolidated these composites by spark plasma sintering at 1800 °C and the hardness and fracture toughness values of these two composites achieved up to 16.70±0.4 GPa, 5.0±0.3 MPam$^{1/2}$ and 16.90±0.2 GPa, 5.9±0.5 MPa·m$^{1/2}$, respectively [44]. C. Yue et al. added 1 wt.% boron nitride nanotube (BNNT)- boron nitride nanoplatelets (BNNP) in ZrB$_2$-SiC (20 vol.%) composite and the hardness, fracture toughness and Young modulus values achieved upto 16.50±1.38 GPa, 4.64±0.36 MPa·m$^{1/2}$, and 441±24 GPa, respectively [45]. W. M. Guo et al. consolidated ZrB$_2$-SiC (20 vol.%)-Yb$_2$O$_3$(5 vol.%) composite by SPS at 1900 °C for 4 min in vacuum and the hardness, fracture toughness and flexural strength values achieved up to 17.30±0.30 GPa, 3.51±0.01 MPa·m$^{1/2}$, and 687±30 MPa, respectively [46]. In this SPS process, the minor phases i.e Yb$_2$Zr$_8$O$_{19}$ and YbBO$_3$ were formed. X. Zhang et al. reported that ZrB$_2$-15 vol.% SiC and ZrB$_2$-30 vol.% SiC ceramic composites were fabricated by spark plasma sintering at 1375°C in vacuum under a uniaxial load of 25 MPa and the results showed that all the composites showed high hardness (10.50-11.10 GPa), high flexural strength (335.50- 391.60 MPa) and low mass ablation rate (0.115- 0.261 mg/cm$^2$·s) [47]. H. Wang et al. fabricated (Zr,Hf)B$_2$-SiC nanostructured composites by high energy ball milling and reactive spark plasma sintering (RSPS) of HfB$_2$, ZrSi$_2$, B$_4$C, and C powders and the flexural strength and fracture toughness values achieved upto 641 MPa and 5.36 MPa·m$^{1/2}$, respectively [48]. The improvement of mechanical properties was largely attributed to their ultra-fine microstructure. M.A. Yan et al. consolidated ZrB$_2$-SiC composite by SPS technique at 1800 °C for 5 min under a pressure of 40 MPa and the bending strength achieved upto 310 MPa [49]. The apparent porosity of ZrB$_2$-SiC composite was very low that indicated SiC was easier to sinter in ZrB$_2$ system. W. W. Wu et al. reported that ZrB$_2$-MoSi$_2$ ceramics were fabricated by slip casting in a strong magnetic field alignment followed by spark plasma sintering at 1700 °C. It was observed that the c-axis of the platelet-like ZrB$_2$ grains aligned parallel to the magnetic field direction with a preferred grain growth

direction along the a, b-axis and experimental results showed a anisotropic properties along the all a, b, and c-axis and the highest Vickers' hardness, but low Young's modulus values were observed in the c-axis direction [50]. S. Wang et al. fabricated $ZrB_2$-SiC nano-composite toughened by $ZrO_2$ fiber by spark plasma sintering at 1700 °C and the fracture toughness of the composites very much improved to a maximum value of 6.56±0.3 MPam$^{1/2}$ by the addition of 15 mass% of $ZrO_2$ fiber [51]. It was observed that some micro-cracks were induced by the phase transformation from t-$ZrO_2$ to m-$ZrO_2$, which was also an important reason behind the improvement in toughness. E. Z. Solvas et al. consolidated $ZrB_2$- 20 vol.% SiC - (0-2 wt.%) $La_2O_3$ composites by SPS technique at 1950 °C and it was reported that $ZrB_2$ with 20 vol.% SiC had room temperature strength of 700±90 MPa, fracture toughness of 6.4±0.6 MPa, Vickers hardness at 9.8 N load of 21.1±0.6 GPa, 1400 °C strength of 400±30 MPa and room temperature strength after 1 h oxidation at 1400 °C of 678±15 MPa. Additionally, 2 wt.% $La_2O_3$ addition to the composite slightly reduced the mechanical performance while increasing tolerance to property degradation after oxidation [52]. G. Daoliang et al. reported that $ZrB_2$-Cu (15 wt.%) composite was prepared by SPS at 1650 °C and the hardness, fracture toughness and bending strength achieved upto 10.16 GPa, 7.0 MPa·m$^{1/2}$, and 593.33 MPa, respectively [53]. J. Song et al. consolidated $ZrB_2$-YAG composite by SPS at 1700 °C and the fracture toughness and Young's modulus achieved upto 3.76 MPa·m$^{1/2}$ and 630 GPa, respectively [54]. It was observed that YAG retained at the grain boundary region which promoted densification and also improved oxidation resistance. J. Zou et al. sintered $ZrB_2$-SiC-BN (ZSN) composites by SPS technique at 1850 °C and the hardness, *E* modulus, *G* modulus, flexural strength, and Poisson ratio achieved in the range of 9.38-9.67 GPa, 250.2-253.1 GPa, 107.9-108.3 GPa, 393.5-472.6 MPa, and 0.158-0.164, respectively [55]. It was reported that the loading strategy plays an important role on the microstructure homogeneity and mechanical properties of the composite. J.Y. Jung et al. consolidated $ZrB_2$ after addition of $Al_3BC_3$ (5 wt.%) and the relative density, hardness and fracture toughness of sintered composite were 99.9%, 20.04 GPa and 3.37 MPa·m$^{1/2}$, respectively [56]. Q. Guo et al. reported that with the increase in $Zr_2Al_4C_5$ content in $ZrB_2$-SiC composites, both of Vicker's hardness and fracture toughness of composites firstly increase and then gradually decrease, and Young's modulus decreases linearly. The optimum values of Young's

modulus, Vickers' hardness and fracture toughness of the composite with 20 vol.% $Zr_2Al_4C_5$ were 440.28 GPa, 18.88 GPa, and 5.31 MPa·m$^{1/2}$, respectively [57]. The improvement of mechanical properties mainly attributed to the layered phase toughening and the homogeneous distribution of in situ formed Zr-Al-C phases. G. B. Yadhukulakrishnan et al. consolidated zirconium diboride reinforced with silicon carbide and multi-walled carbon nanotube at 1900°C and the hardness, fracture toughness and flexural strength values of the composites varied from 14.17-22.71 GPa, 1.53-3.53 MPa·m$^{1/2}$, and 301-553 MPa, respectively [58]. Reinforcement of SiC and CNT improved the indentation fracture toughness of the composites through toughening mechanisms. N. Gupta et al. consolidated near theoretical densification of $ZrB_2$-18 wt.% SiC is achievable with the addition of 5 wt.%$TiSi_2$ via SPS at a temperature of 1600 °C and pressure of 50 MPa for 10 min and possessed excellent hardness (~20 GPa) and indentation toughness (~5 MPa·m$^{1/2}$) [59]. Liquid phase sintering in the presence of $TiSi_2$ improved the sinterability and also enhanced the mechanical properties. I. Akin et al. prepared $ZrB_2$-ZrC-SiC composites by spark plasma sintering at temperatures of 1750 °C for 300 s under a pressure of 40 MPa and $ZrB_2$ (60 vol. %)-ZrC (20 vol.%)-SiC (20 vol.%) composite had the highest values of hardness and fracture toughness (21.10±0.30 GPa and 5.46±0.22 MPa m$^{1/2}$, respectively) [60]. Zigzag crack mode resulted remarkable crack deflections and the high fracture toughness value. C. Hu et al. fabricated $ZrB_2$-SiC composite at 1800 °C by spark plasma sintering using $TaSi_2$ as sintering aid and Vickers hardness and fracture toughness of $ZrB_2$-SiC composites showed an increasing tendency from 16.9 to 20.2 GPa and 3.70 to 4.44 MPa·m$^{1/2}$, respectively with increasing SiC content. Moreover, elastic moduli of composites declined from 464.8 to 453.2 GPa with increasing SiC [61]. S. Guicciardi et al. fabricated $ZrB_2$ composites containing 10, 20 vol.% of SiC whiskers and 20 vol.% of SiC-chopped fibers by spark plasma sintering at 1500 °C and it was observed that addition of SiC whiskers promoted both strengthening and toughening compared with respect to pure $ZrB_2$ [62]. The theoretical model clearly indicated that the toughness increased by crack deflection in the whisker-reinforced composites and by crack bowing in the fiber-reinforced composite. D. Sciti et al. consolidated $ZrB_2$ with the addition of 1, 3, and 9 vol% $MoSi_2$ as sintering aid by SPS within 1700-1900 °C and achieved high hardness (18.2±0.7 GPa) and fracture toughness (4.0±0.6 MPa·m$^{1/2}$) values at sintering temperatures

around 300-400 °C lower than those needed for the pure ZrB$_2$ with consequent refinement of the microstructure [63]. R. Licheri et al. synthesed ZrB$_2$-40 vol.% ZrC-12 vol.% SiC powders by self-propagating high-temperature synthesis and subsequently consolidating them by spark plasma sintering and had a Vickers' hardness of 16.9±0.2 GPa and a fracture toughness of 5.9±0.5 MPa·m$^{1/2}$ [64]. H. Wang et al. prepared zirconium diboride reinforced by nano-SiC whiskers by spark plasma sintering at 1550 °C and found that the flexural strength and fracture toughness of the composites were improved from 416 MPa for monolithic ZrB$_2$ to over 545 MPa for ZrB$_2$-15 vol.% SiC$_w$ composites and from 5.46 MPa·m$^{1/2}$ to more than 6.81 MPa·m$^{1/2}$ in the same composition range [65]. The mechanical properties were further improved by adding sintering aids like AlN and Si$_3$N$_4$. T. Tsuchida et al. synthesized ZrB$_2$-ZrC precursor powders by Mechanical activation-assisted self-propagating high-temperature synthesis (MA-SHS) technique and then consolidated by spark plasma sintering (SPS) at 1800 °C resulting fine and homogeneous microstructure composed of less than 5 micron grains. The Vickers hardness and fracture toughness values achieved in the range of 13.6-17.8 GPa and of 2.9-5.1 MPa·m$^{1/2}$, depending on the molar ratio of ZrB$_2$/ZrC [66]. K. H. Kim et al. sintered La doped ZrB$_2$-ZrC composites by SPS and it was found that fracture toughness of the lanthanum-containing ZrB$_2$-ZrC was about 2.56 MPa·m$^{1/2}$, which was comparable to that of the pure composite [67]. C. Hu et al. consolidated (Zr,Ti)B$_2$-(Zr,Ti)N composites by spark plasma sintering using ZrB$_2$ and TiN powders as the starting materials and it was observed that above 1900 °C sintering, the solid solution of (Zr,Ti)N reached saturation in all the composites. The achieved hardness, fracture toughness, Young's modulus, shear modulus and poisson ratio were in the range of 16.7-19.2 GPa, 2.42-4.76 MPa·m$^{1/2}$, 350-474 GPa, 151-206 GPa, and 0.14-0.17, respectively [68]. A. Snyder et al. studied the effects in ZrB$_2$-SiC-ZrC composites with four different compositions were investigated via spark plasma sintering at 1800 °C and found that higher percentage of SiC resulted in grain growth inhibition, and increased Rockwell A hardness and strength of the composite [69]. T. Tsuchida et al. synthesized ZrB$_2$-ZrC powder from Mechanical activation-assisted self-propagating high-temperature synthesis (MA-SHS) technique and consolidated by spark plasma sintering at 1800 °C and exhibited fine, homogeneous microstructure and the Vickers hardness and fracture toughness values achieved upto 17.8 GPa of 3.8 MPa·m$^{1/2}$, respectively [70]. S. Chakraborty et

al. reported that ZrB$_2$-SiC$_p$ (w/w 80:20) composites were spark plasma sintered at three different temperatures (1900, 2000 and 2100 °C) and SiC was obtained by in situ pyrolysis of polycarbosilane during sintering [71]. The Vickers' micro-hardness, fracture toughness of the ZrB$_2$-SiC$_p$ composite sintered at 2000 °C achieved upto 16.22 GPa and 3.69 MPa·m$^{1/2}$, respectively and wear resistance coefficient and wear rate values of all the composites were found to be very low. M. Cao et al. consolidated ZrB$_2$-based nano-composite by enforcing with nanosized SiC by spark plasma sintering and the densification and fracture toughness were improved to 97.70% and 8.205 MPa·m$^{1/2}$ by introducing 5 mass% nano-sized SiC with particle size of 20 nm [72]. The major papers are focused on sintering and densification of different ZrB$_2$-based composite by spark plasma sintering technique at different temperatures, soaking time and pressure and also the effect of microstructural aspect (homogeneity, grain size and distribution) between ZrB$_2$ and secondary grains and their interfaces towards densification, structural, electrical and thermal properties. However, further research is necessary in details to determine the effect of additional sintering parameters, such as pulse ON-OFF rate, heating rate, loading rate on the composites properties.

## 4. CONCLUDING REMARKS

Boride of zirconium (ZrB$_2$) is a unique non-oxide ceramic material for ultra high temperature aerospace application like hypersonic re-entry vehicles, rocket nozzles, jet-vanes, space shuttles and also other conventional applications like thermal, nuclear power plant, high temperature crucible, plasma fusion electrodes etc. For making real life desired shaped components, proper sintering and defect free compaction either in bulk form or coating form is necessary. From the above review sintering and consolidation of ZrB$_2$, following conclusions may be drawn:

For developing high density and pore free compact, spark plasma sintering is a most cost effective technique for obtaining dense ZrB$_2$ sample. The spark plasma sintering is based on the dc electrical discharge phenomenon under high current and low voltage mode which generates spark plasma at localized region and sintering can take place by optimum thermal and electrolytic diffusion mechanism. But this SPS technique is limited to simple geometry and complex shapes and moreover, bigger samples cannot be made. Metallic additive (Cu) and low melting phases (MoSi$_2$, TaSi$_2$) have been

used to promote liquid phase formation that enhances densification by facilitating particle rearrangement and mass transport at relatively lower temperature. However, the limitation of the addition of these low melting additives is that they deteriorate the high temperature structural properties. Currently, different ceramics that include silicon carbide, boron nitride, zirconium carbide, $Al_3BC_3$, $Zr_2Al_4C_5$, graphene, ytterbium oxide, lanthanum oxide, yttrium aluminium garnet, zirconia and others in different forms and shapes are being used as additives to improve the densification of monolithic $ZrB_2$. Besides enhancing the densification, these additives also improve the high temperature structural properties of $ZrB_2$ ceramics.

## ACKNOWLEDGMENTS

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