An investigation on thermal shock resistance of ZrB$_2$–SiC composites

Bahador Abolfathnezhad, Zohre Balak* and Mahdi Azizieh

Department of Materials Science and Engineering, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran

* Author to whom any correspondence should be addressed.

E-mail: zbalak1983@gmail.com

Keywords: thermal shock resistance, ZrB$_2$–SiC, Nano–SiC, SPS

Abstract

In this research, the effect of particle size of the SiC powder was studied on the thermal resistance. In this regard, initial SiC powder was prepared in three sizes of 25 $\mu$m, 45 nm, and 80 nm. The sintering of the composites was performed at three temperatures of 1600 °C, 1700 °C, and 1800 °C, as well as at three times of 4 min, 8 min, and 12 min under the constant pressure of 40 MPa. The thermal shock resistance of the sample was investigated through fast cooling in water. Moreover, the flexural strength of the samples was measured through the three-point method. The results showed that the thermal shock resistance is improved by declining the particle size of initial SiC from micro to nano in such a way that the amount of the critical $\Delta T$ for the samples sintered at 1700 °C and 1800 °C reaches 510 °C and 590 °C. The flexural strength reaches the highest value (about 400 MPa) using nano scale SiC particles.

1. Introduction

Today, the need for novel materials that can endure temperatures higher than 2000 °C for a long time in addition to the functionality in the oxidizing and corrosive atmosphere is necessary. Besides, sharp edges and surfaces can be employed in order to improve the aerodynamics level of ultrasonic carriers, re-entry aircraft, propulsions, and so on. The implementation of these types of designs requires high capabilities materials in various operational mediums like oxidizing atmosphere at high temperatures and corrosive gas at high speeds. Nowadays, there are a limited number of materials meeting these capabilities. To solve this problem, ultra-high temperature ceramics (UHTCs), which are known as an advanced group of materials, have been at the center of interest due to their attractive properties. Ultra-high temperature ceramics belong to one of the refractory material groups, including metallic borides, carbides, and nitrides [1–10].

Good oxidation resistance and high thermal and electrical conductivity of diboride refractory compositions compared to the other intermetallic compounds (carbides and nitrides) have been led to an extensive investigation on the transition metal diborides from the fourth to the fifth group of the periodic table (Ti, Zr, Hf, Nb, Ta) [7, 11, 12].

Borides and carbides such as TiB$_2$, TiC, NbC, and NbB$_2$ also form several compounds like TiO$_2$ and Nb$_2$O$_3$ with a temperature lower than 2000 °C, which will be not usable [13]. Among diborides, ZrB$_2$–based ceramics have been at the center of interest because of their exclusive compositions with relatively low density, good electrical and thermal conduction, high hardness, high melting temperature, good thermal shock resistance, and excellent chemical and mechanical stability at high temperatures [5–7].

However, extensive investigations have been implemented in order to improve the oxidation and shockability of this ceramic at high temperatures. Zimerman et al reported that the addition of 30 vol% SiC substantially improves thermal shock resistance [14]. The triple system of ZrB$_2$–SiC–G (ZSG), as a suitable shock resistance system, has been studied by various researchers [15–17]. Additionally, the manufacture of ZrB$_2$ porous ceramics, layered composites, and using a secondary phase like ZrO$_2$ [18–21], which suffers a phase change during applying a thermal cycle, are of the research works conducted to improve the shock resistance of this ceramic. The addition of Al$_3$B improves shockability up to 600 °C in addition to improving sinterability and fracture toughness [22]. The manufacturing parameters like milling time and sintering conditions also
significantly affect shockability so that the critical temperature difference increases from 580 °C to 650 °C by increasing time from 3 to 15 h \cite{23}. The effect of additives like MoSi2, SiC, HfB2, and carbon fiber along with manufacturing parameters on the shock resistance has been examined using an experiment designed by the Taguchi method \cite{24}.

Different methods have been used in order to study the shock resistance behavior thus far; they are categorized into two groups of applying shock during heating and cooling, which are carried out through electrical resistance and cooling in water, respectively. The second method is the simplest one \cite{17} that was utilized in this research.

According to the results obtained from the effect of milling time in previous research works, we tried to improve shock resistance using initial SiC nanoparticles.

### 2. Experimental procedure

Table 1 presents the primary characteristics of SiC and ZrB2 powders used in this research. For each composite sample, the powders were dispersed and mixed based on the values obtained from rule mixture composites based on ZrB2–30 Vol% SiC. In order to reduce the particle size and create better mixing with additives, the mixture of the powders was milled by a planetary mill with a speed of 200 rpm for 3 h after dispersion. Milling was performed in an ethanol medium because of the possibility of oxygen adsorption in the surface powder particles.

After milling, the powders were dried and the resulted powder mixture coated into the cylindrical graphite mold by a graphite layer was charged and was then located into the SPS container. The SPS process was carried out using an SPS device (model: SPS-20T-10) at different temperatures, times, and pressures (table 2). After the SPS process, a polishing process was accomplished with a diamond stone to remove the graphite layer on the surface of the samples.

The samples were cut to a thickness of 0.1 mm by wire-cut to perform mechanical properties, shockability, and microstructure studies. To determine the density, three slices were cutted from each sample and their relative density and open porosity percent were measured by the Archimedes method. To evaluate the shockability, the samples were heated into a furnace up to the temperatures of 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, 650 °C, and 700 °C and held for 20 min 25 °C. For each samples, five bars were quenched into water held at the temperature of 25 °C and an average retained strength was calculated and reported. The flexural strength of the samples was determined through the 3-point bending test (five bars for each sample) and the results compared with those of un-heated (original) samples. Scanning electron microscopy (SEM) was employed to investigate the microstructure of the samples.

### Table 1. The primary characteristics of SiC and ZrB2 powders.

| Type   | Particle size | Company                                      |
|--------|---------------|----------------------------------------------|
| ZrB2   | 20 μm         | Northwest Institute for Non-Ferrous Metal Research, China, 99.5% purity |
| SiC    | 25 μm         | Northwest Institute for Non-Ferrous Metal Research, China, 98.7% purity |
| SiC    | 80 nm         | Northwest Institute for Non-Ferrous Metal Research, China, 98.7% purity |
| SiC    | 45 nm         | Northwest Institute for Non-Ferrous Metal Research, China, 98.7% purity |

### Table 2. The conditions of SPS for each sample.

| Sam. code | SiC particle Size | Time (min) | Temp. (°C) | Press. (MPa) |
|-----------|-------------------|------------|------------|--------------|
| 1         | 25 μm             | 4          | 1700       | 40           |
| 2         | 25 μm             | 4          | 1800       | 40           |
| 3         | 45 nm             | 4          | 1700       | 40           |
| 4         | 45 nm             | 4          | 1800       | 40           |
| 5         | 45 nm             | 8          | 1800       | 40           |
| 6         | 45 nm             | 12         | 1800       | 40           |
| 7         | 45 nm             | 4          | 1600       | 40           |
| 8         | 80 nm             | 4          | 1700       | 40           |
| 9         | 80 nm             | 4          | 1800       | 40           |
Moreover, there are high residual stresses in the interface of the transgranular nanoparticles and matrix grains so it hinders the grain growth. The reduction of the grain size along with sinterability improvement lead to reported that the SiC intergranular particles with a size of lower than 1.345 nm. The scale nanoparticles brings about improving sinterability and reducing the size of the composite grains. Liu [26] studied the effect of SiC nanoparticles on the microstructure and mechanical properties of ZrB2. The particle size of ZrB2 and SiC initial powders used in this research were 2 µm and 30 nm, respectively. The powder mixture was sintered at 1900 °C for 30 min under a pressure of 30 MPa by the hot press (HP) method. They reported that the SiC intergranular particles with a size of lower than 1 µm play a key role in locking boundaries, so it hinders the grain growth. The reduction of the grain size along with sinterability improvement lead to increasing flexural strength in the samples having nano-scale SiC particles compared to micro-scale SiC ones. Moreover, there are high residual stresses in the interface of the transgranular nanoparticles and matrix grains (sub-interfaces) due to the presence of transgranular nanostructures, which can lead to the formation of the sub-grain boundary. Due to these sub-grain boundaries, a huge amount of fracture energy is consumed during the flexural strength tests and consequently leads to improving flexural strength [26].

### 3. Results and discussion

#### 3.1. Mechanical properties

The grain size of the composite, the relative density, and the open porosity percent of the sintered samples are presented in table 3. The microstructure analysis was given in the previous work [22, 23].

| Sam. code | SiC particle Size | Grain size SiC | Grain size ZrB2 | Relative density(%) | Porosity(%) |
|-----------|------------------|---------------|----------------|--------------------|-------------|
| 1         | 25 µm            | 4.2 µm        | 4.3 µm         | 75.3               | 24.4        |
| 2         | 25 µm            | 5.8 µm        | 7.1 µm         | 85                 | 14.6        |
| 3         | 45 nm            | 3.2 µm        | 3.8 µm         | 83.7               | 17.3        |
| 4         | 45 nm            | 3.8 µm        | 4.9 µm         | 92.9               | 7.43        |
| 5         | 45 nm            | 3.9 µm        | 5.0 µm         | 95.2               | 6.2         |
| 6         | 45 nm            | 4.1 µm        | 6.1 µm         | 97.6               | 3.8         |
| 7         | 45 nm            | 2.1 µm        | 3.3 µm         | 79.2               | 20.2        |
| 8         | 80 nm            | 3.1 µm        | 4.1 µm         | 82.9               | 17.4        |
| 9         | 80 nm            | 3.7 µm        | 5.3 µm         | 98.8               | 2.8         |

#### 3.2. Shockability

Thermal shock means the resistance to failure resulted from the temperature changes applied to the material, or in other words, cracking in the material owing to the thermal stress initiated from severe temperature changes; ceramics and glass segments are prone to this type of fracture owing to low toughness, low thermal conduction, and high thermal expansion coefficient [27–29].
Temperature difference and stresses created lead to making a crack on the surface of ceramic material, resulting in the fracture of the sample with its growth and propagation [27–29].

The fracture of the sample, which is initiated from thermal shock, can be controlled by the following factors:

1. Reduction of material thermal gradient (through slower applying temperature changes),
2. Reduction of material thermal expansion coefficient,
3. Increase of material strength,
4. Heat treatment and stress relief,
5. Reduction of Young’s modulus, and
6. Increase of toughness (control of crack) [27–29].

In order to investigate the effect of temperature, sintering time, and SiC particle size on thermal shock resistance, at first, the residual
flexural strength graphs in terms of $\Delta T$ were drawn separately for sample separately (see figure 2(a)) and were analyzed in the next sections.

It is clear, applying higher temperature difference values lead to declining flexural strength, which is initiated from residual stresses created. Obtaining the critical temperature of the shockability is expressed for sample No. 1. For this purpose, the point which the flexural strength reaches to 70% of its initial value is discernible and from there a line is drawn on the $X$-axis; the intersection location with the $X$-axis displays the critical temperature difference of the shockability, which is equal to 480 °C.
3.2.1. Effect of sintering temperature on thermal shock resistance

To investigate the effect of sintering temperature on the thermal shock resistance, the samples No. 7, 3, and 9 (sintering temperature: 1600 °C, 1700 °C, and 1800 °C; sintering time: 4 min; SiC particle size: 45 nm; sintering pressure: 40 MPa) were compared. As shown in figure 3, the thermal shock resistance increases by increasing the sintering temperature.

The size of the SiC grains increases from 2.1 to 4 μm by increasing the sintering temperature from 1600 °C to 1800 °C. The studies reveal that the finer grain microstructures indicate better shock resistance from themselves [20]. However, it is observed that increasing the sintering temperature results in a dramatic improvement of sinterability and reduction of porosities from 8% to 2%. Porosities act as channels to heat transfer and help to improve shockability. Furthermore, the presence of open porosities leads to consuming crack energy and preventing its propagation in the microstructure, and finally improving fracture toughness through activating the toughening mechanisms (entrapping cracks in porosities). According to that fracture toughness has a direct relation with shockability [27, 28] (see figure 4), and also the information presented in sections 3–4, it can be concluded that the presence of porosities is a positive factor for improving shockability. It should be paid attention to the amount of porosities available in the microstructure. Due to the high amount of porosities in the samples sintered at 1600 °C and 1700 °C and the lower initial flexural strength of these samples compared to the sample sintered at 1800 °C, the thermal shock resistance of these samples are lower.

3.2.2. Effect of sintering time on thermal shock resistance

To investigate the effect of sintering time on the thermal shock resistance, samples No. 4, 5, and 6 (sintering temperature: 1800 °C; SiC particle size: 45 nm; sintering pressure: 40 MPa) were compared. As can be seen in figure 5, thermal shock resistance decreases by increasing sintering time. An investigation on the graphs of grain
size and open porosity percent of these samples indicates the increase of grain size and the decrease of open porosity percent by increasing sintering temperature.

3.2.3. Effect of SiC grain size on thermal shock resistance
The effect of SiC particle size on the thermal shock resistance at two temperatures of 1700 °C and 1800 °C is presented in figure 6. As seen, thermal shock resistance has an upward trend by decreasing particle size in both temperatures; this increase is more evident at 1800 °C. Thermal shock resistance decreases by reason of the constant percent of the porosity in this range on one hand and the increase of the grain size on the other. By examining the trend of microstructural and density changes of these samples using the data presented in table 3, it is observed that the grain size of the resulted composite decreases about 1 μm at both temperatures by decreasing initial particle size (from 4.2 to 3.2 for 1700 °C and from 4.4 to 3.8 for 1800 °C) while the percent of the porosities in the samples sintered at 1800 °C and 1700 °C reaches 7% and 17%, respectively. On the other hand, the high amount of porosities leads to decreasing the initial flexural strength, fracture toughness, and finally shock resistance.
4. Conclusion

ZrB$_2$–30 vol% SiC were fabricated by SPS using different initial SiC particle size successfully. It was cleared that the shockability improved by sintering temperature up to 1800 °C. In fact in this temperature, desirable microstructure with good combination of grain size and relative density was achieved. Raising the holding time of SPS at the temperature of 1800 °C, the shockability decreased continuously. It means both coarsening the grain size and reaching to nearly full relative density are detrimental for shockability. Finally, it was found that using finer initial SiC powder in nano scale (from 25 μm to 40 nm) significantly improves the shockability especially at the upper temperature (1800 °C in comparison with 1700 °C).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Zohre Balak  https://orcid.org/0000-0003-4232-1462
References

[1] He Z and Fu J 2021 3D characterization of the SiC nanoparticle distribution in ZrB2–SiC ceramics with synchrotron x-ray nanoscale computed tomography Ceram. Int. 47 12780–8
[2] Farahbakhsh I, Ahmadi Z and Shahedi Asl M 2017 Densification, microstructure and mechanical properties of hot pressed ZrB2–SiC ceramic doped with nano-sized carbon black Mater. Charact. 135 7717–22
[3] Haghgoosei Shafagh S, Iafaghrolinejad S and Javadian S 2021 Beneficial effect of low BN additive on densification and mechanical properties of hot-pressed ZrB2–SiC composites Synthesis and Sintering 109–75
[4] FarahBakhsh I, Antiochia R and Jang H W 2021 Pressureless sinterability study of ZrB2–SiC composites containing hexagonal BN and phenolic resin additives Synthesis and Sintering 199–104
[5] Pages 8411–8417 Xiaqiang F et al 2019 Investigation of pressureless sintered ZrB2-based ceramics Ceram. Int. 45 7717–22
[6] Chen Z B et al Synthesis of rod-like ZrB2 crystals by boro/carbothermal reduction, , Ceram. Int. 45 2019 13726–31
[7] Karimirad S and Balak Z 2019 Characteristics of spark plasma sintered ZrB2–SiC–SiCp composites Ceram. Int. 45 6275–81
[8] Grigoriev O, Nespor I, Vedel D, Mosina T and Silverstoni L 2021 Influence of chromium diboride on the oxidation resistance of ZrB2–MoSi2 and ZrB2–SiC ceramics J. Eur. Ceram. Soc. 41 2207–14
[9] Zhao X T, Shao G, Feng L, Wang H L, Fan B B, Lu H X, Xu H L, Chen D L and Zhang R 2017 ZrB2–SiCw ceramic composites synthesized by in situ reaction and spark plasma sintering Int. J. Appl. Ceram. Technol. 14 485–50
[10] Xuanru R, Chu H, Wu K, Zhang A, Huang M, Ma C, Liu H and Feng P 2021 Effect of the ZrB2 content on the oxygen blocking ability of ZrB2–SiC coating at 1973K J. Eur. Ceram. Soc. 41 1059–70
[11] Rezapour A and Balak Z 2020 Fracture toughness and hardness investigation in ZrB2–SiC–Zr composite Mater. Chem. Phys. 241 122284
[12] Shahedi Asl M, Zamharir M J, Ahmadi Z and Parvizi S 2018 Effects of nano-graphite content on the characteristics of spark plasma sintered ZrB2–SiC composites Mater. Sci. Eng. A 716 99–106
[13] Germi M D, Mahaseni Z H, Ahmadi Z and Shahedi Asl M 2018 Phase evolution during spark plasma sintering of novel Si3N4-doped TiB2–SiC composite Mater. Charact. 145 225–32
[14] Shahedi Asl M, Neyebi B, Motalebbezadeh A and Shokouhimehr M 2019 Nanoindentation and nanostructural characterization of ZrB2–SiC composite doped with graphite nano-flakes Composites Part B: Engineering 175 107153
[15] Pourmahmmonad Vafa N, Ghassemi Kakhroudi M and Shahedi Asl M 2020 Advantages and disadvantages of graphite addition on the characteristics of hot-pressed ZrB2–SiC composites Ceram. Int. 46 6561–6
[16] Shahedi Asl M, Pazhoushanfar Y, Sabahi Namini A, Shaddel S, Fattahi M and Mohammadi M 2020 Role of graphite nano-flakes on the characteristics of ZrB2–SiC-based composites reinforced with SiC whiskers Diam. Relat. Mater. 105 107786
[17] Wang A, Hu P, Du B, Fang C, Zhang D and Zhang X 2018 Cracking behavior of ZrB2–SiC Graphite sharp leading edges during thermal shock Ceram. Int. 44 7694–9
[18] Jin X, Dong L, Li Q, Tang H, Li N and Qu Q 2016 Thermal shock cracking of porous ZrB2–SiC ceramics, Ceram. Int. 42 13309–13
[19] Zhang L, Wei C, Li S, Wen G, Liu Y and Wang P 2019 Mechanical and thermal shock properties of laminated ZrB2–SiC/SiC ceramics, Ceram. Int. 45 6503–8
[20] Li W, Zhang X, Hong C, Han W and Han J 2009 Preparation, microstructure and mechanical properties of ZrB2–ZrO2 ceramics J. Eur. Ceram. Soc. 29 779–86
[21] Wang S B, Li Y and Zhang X H 2013 Influence of the microstructure evolution of ZrO2 fiber on the fracture toughness of ZrB2–SiC nanocomposite ceramics Mater. Des. 49 808–13
[22] Zhao X, Chen Z, Wang H, Zhang Z, Shao G, Zhang R, Fan B, Lu H, Xu H and Chen D 2020 The influence of additive and temperature on thermal shock resistance of ZrB2 based composites fabricated by Spark Plasma Sintering Mater. Chem. Phys. 240 122061
[23] Akhlaghi N, Balak I Z and Najafi Birgani E 2019 Milling time and sintering parameters optimization to fabricate ZrB2–30 vol% SiC composite with highest thermal shock resistance Mater. Res. Express 6 055606
[24] Balak Z, Asizheh M, Kafashan H, Shahedi Asl M and Ahmadi Z 2017 Optimization of effective parameters on thermal shock resistance of ZrB2–SiC-based composites prepared by SPS using taguchi design Mater. Chem. Phys. 196 333–40
[25] Darhaki F, Balak Z and Etemadmi R 2019 Effect of nano and micro SiC particles on the microstructure and fracture toughness of ZrB2–SiC nanocomposite produced by SPS method Mater. Res. Express 6 095608
[26] Shahedi Asl M, Ahmadi Z, Parvizi S, Balak Z and Farahbakhsh I 2017 Contribution of SiC particle size and spark plasma sintering conditions on grain growth and hardness of TiB2 composites Ceram. Int. 43 13924–31
[27] Etemadmi R and Balak Z 2019 Investigating the effect of SPS parameters on spark plasma sintering and fracture toughness of ZrB2–SiC nanocomposite Ceram. Int. 45 4763–70
[28] Monteverde F, Melandri C and Guicciardi S 2006 Microstructure and mechanical properties of an HfB2 + 30 vol% SiC composite consolidated by spark plasma sintering Mater. Chem. Phys. 100 513–9
[29] Liu Q, Han W, Zhang X, Wang S and Han J 2009 Microstructure and mechanical properties of ZrB2–SiC composites Mater. Lett. 63 1322–5