Synergistic influence of SiC and C₃N₄ reinforcements on the characteristics of ZrB₂-based composites

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ABSTRACT
In this work, ZrB₂–SiC and novel C₃N₄-doped ZrB₂–SiC composites were manufactured at 1850°C under an external load of 40 MPa for 6 min via spark plasma sintering. The effects of C₃N₄ on the mechanical characteristics (flexural strength, Vickers hardness, and fracture toughness) and microstructure of the ZrB₂–SiC-based composites were investigated. By adding 5 wt% g-C₃N₄, a fully dense ceramic composite was fabricated, compared to the C₃N₄-free ZrB₂–SiC composite with a relative density of 95%. Removal of ZrO₂ and B₂O₃ from the surface of ZrB₂ particles via chemical reactions with C₃N₄, and the in-situ synthesis of ZrC and BN as new phases were studied by XRD and SEM analyses. Indentation fracture toughness, flexural strength, and Vickers hardness improved from 4.5 MPa.m¹/₂, 460.2 MPa and 17.4 GPa to 6.1 MPa.m¹/₂, 580.2 MPa and 21.2 GPa, respectively, by adding g-C₃N₄ to the ZrB₂–SiC ceramic.

1. Introduction
Ultrahigh temperature ceramics (UHTCs) are broadly used in structural parts under harsh conditions and high-temperature applications because of their amazing properties like high melting point (>3000°C), excellent oxidation resistance, high thermal conductivity, and good corrosion resistance [1–5]. As a member of UHTCs, ZrB₂ has gained a great deal of scientific attention owing to the attractive physical and mechanical characteristics, including relatively low density, high melting temperature, good electrical and thermal conductivity, high modulus and strength, and chemical stability [6–9]. However, this material suffers from some deficiencies like weak sinterability, undesirable oxidation resistance at high temperatures, oxide impurities formation on its surface, and low bulk self-diffusion coefficient [8,10–13]. Therefore, it is necessary to apply very high temperatures and external mechanical loads for manufacturing the fully dense monolithic ZrB₂ [14–16].

In the last decades, scientists have focused on solving these shortcomings of ZrB₂-based UHTCs. They found that SiC addition to ZrB₂ not only enhances the sinterability and mechanical properties by minimizing the grain growth, but also leads to the oxidation resistance enhancement by the formation of borosilicate glassy layers [17–20]. Therefore, ZrB₂–SiC ceramic composites have been studied by many researchers and several manufacturing techniques like reactive hot pressing (RHP), microwave sintering (MS), spark plasma sintering (SPS), pressureless sintering (PS), and hot pressing (HP) have been considered. Pressureless sintering is a consolidation method that manufactures complex-shaped components at relatively low cost without applying an external pressure [21,22], while fully dense ZrB₂-based ceramic materials can be densified by HP, RHP, and SPS [16,23]. Spark plasma sintering is recognized as a modern fabrication method to prepare the fully dense metals, ceramics, and polymers by applying a direct or pulsed current to the powders simultaneously with an uniaxial mechanical load. Compared to the conventional sintering methods, lower temperatures and shorter holding times are required in the SPS process, which assist obtaining finer microstructures [24].

Generally, using a sintering aid in UHTC matrix composites can encourage the densification and improve the thermo-mechanical feathers. According to their role, additives are categorized into three following types [25]: (1) Nitrides, carbides, and carbon allotropes which can remove the surface oxide impurities via chemical reactions [25–33]. (2) Metals and disilicides that can enhance the densification through liquid phase formation at elevated temperatures [34–41]. (3) Other components like ZrH₂ and HfH₂ [25]. Participation of BN in a chemical reaction with ZrO₂ contamination led to the densification enhancement in ZrB₂–SiC composites [29,30]. Fully dense ZrB₂–SiC sample was densified by hot pressing by adding 4.5 vol % ZrN or 3 vol% HfN [27,28]. Adding 5 wt% TiN resulted in
in an increase in the relative density of TiB$_2$-based ceramic; such a phenomenon was related to the observation of the trace of in-situ formed nano-sized hexagonal BN secondary phase in grain boundaries [42]. The addition of Si$_3$N$_4$ resulted in the manufacturing of fully dense ZrB$_2$–SiC composites with finer microstructure with layered BN in boundaries [43].

Graphitic carbon nitride (g-C$_3$N$_4$), as a member of polymeric semiconductor materials, has received tremendous attention due to its excellent properties such as nontoxicity, thermal/chemical stability, cheap, and simple preparation methods [44–47]. The combination of these unrivaled characteristics of this semiconductor makes it a suitable material for using in various applications like photoreactivity, carbon dioxide reduction, photocurrent, solar energy, and fuel cells [48–52]. Graphitic C$_3$N$_4$ powder was easily synthesized via one-step calcination of inexpensive organic precursors like thiourea, melamine, urea, and cyanamide having “earth-abundant” elements [53–55]. In our previous research, the role of g-C$_3$N$_4$ additive on the mechanical features and sinterability of ZrB$_2$-based materials was studied for the first time. Introduction of C$_3$N$_4$ in ZrB$_2$ ceramics not only led to the finer microstructure and improved densification via the in-situ formation of ZrC and BN, but also resulted in enhanced mechanical properties when only 5 wt% C$_3$N$_4$ has been added to ZrB$_2$ [56].

The importance of this research is to understand the influence of g-C$_3$N$_4$ additive on the mechanical characteristics, microstructural evolution, and densification behavior of ZrB$_2$–SiC composites. The mechanical features and sintering behavior of ZrB$_2$–SiC and C$_3$N$_4$-doped ZrB$_2$–SiC composites specimens densified at a temperature of 1850°C under a load of 40 MPa for 6 min by SPS, are studied and compared.

2. Experimental protocol

2.1. Materials and processing

In this study, commercial SiC powders (particle size <3 μm, purity >99.0%, Xuzhou Hongwu Co.), ZrB$_2$ powders (particle size <2 μm, purity >99.8%, Xuzhou Hongwu Co.), and prepared C$_3$N$_4$ (synthesized in our laboratory) were selected as starting materials. The C$_3$N$_4$ powder was prepared by calcination of melamine up to 520°C via directly heating in a ceramic crucible [53]. Powder mixtures of ZrB$_2$–SiC (ZS) and ZrB$_2$–SiC–C$_3$N$_4$ (ZSC) composite specimens were weighted based on Table 1. The powders were mixed in an ethanol medium, and then, the obtained slurries were dispersed for 0.5 h in an ultrasonic bath. After that, the slurries were heated and more mixed on a hot-plate magnetic stirrer for 4 h at 140°C, then an oven was used to fully dehumidify the mixtures at 120°C for 720 min. After the drying step, the as-mixed powders were milled in zirconia media and sieved to provide a uniform mixture with minimal agglomeration. Finally, the obtained homogenous composite powders were loaded into a mold made of graphite, covered with flexible graphite foils, to densify disk-shaped samples. The sintering processes were completed in a vacuum SPS furnace (Nanozint 10i, Khala Poushan Felez Co., Iran) for a holding time of 6 min at a temperature of 1850°C under a load of 40 MPa.

2.2. Characterization

The Archimedes technique was applied to the assessment of bulk density. The rule of mixtures was used to calculate the reference density based on the theoretical densities of the initial components in the powder mixture, without considering the formation of any probable in-situ phases during the SPS process. Relative density (RD) was reported as the ratio of the bulk density to the reference density of the sintered samples. Phase composition identification of composites was done by an X-ray diffraction device (XRD: Philips PW1730). Field emission SEM (Mira3, Tescan) and energy dispersive spectroscopy were used for microstructural analysis of the fracture and polished surfaces of the as-prepared composite samples and their elemental identifications, respectively. Also, the HSC Chemistry package was applied for thermodynamics evaluation of possible chemical reactions that occurred during the manufacturing process.

The indentation technique was employed to determine the hardness and fracture toughness utilizing the Vickers diamond pyramid and applying 5 kg (49 N) load for a dwell time of 10 s on the polished section of samples. Indentation fracture toughness (K$_IC$) was assessed by direct measurement of the lengths of crack created by Vickers indenter through the following equation proposed by Anstis [57].

$$K_{IC} = 0.016 \left( \frac{E}{H_v} \right)^{1/2} \left( \frac{L}{C^{1/2}} \right)$$

(1)

where E is the elastic modulus, L is the indentation force, $H_v$ is Vickers hardness, and C is half of the crack length. It should be noted that the radial cracks length was evaluated via an optical microscope. The elastic (Young) modulus was calculated by employing an empirical relation of Nielsen equation (Eq. (2) [58]):

$$E = E_0 \left( \frac{1 - P^2}{1 + \frac{P}{P_0}} \right)$$

(2)

Table 1. Coding system and corresponding composition for each sample.

| Label | Composition       |
|-------|-------------------|
| ZS    | ZrB$_2$–25 vol% SiC |
| ZSC   | ZrB$_2$–25 vol% SiC–5 wt% C$_3$N$_4$ |
where $E_0$, $p$, and $\rho$ are the theoretical Young modulus of the porosity-free specimen, porosity amount, and Nielsen’s shape factor that equals to 0.4, respectively. The values of 500 [59, 60], 410 [60,61], and 377 GPa [62] were considered for Young moduli of ZrB$_2$, SiC, and g-C$_3$N$_4$, respectively. The flexural strength of the as-sintered samples, with dimensions of 1.5 $\times$ 2 $\times$ 25 mm$^3$, was tested by a three-point bending test (ASTM C-1161-02 C). A fixed gauge length of 20 mm and a constant loading speed of crosshead equal to 0.2 mm/min were employed at room temperature.

### 3. Results and discussion

Figure 1 displays the FESEM images of the polished sections of as-SPSed ZS and ZSC composites. Compared to the monolithic ZrB$_2$ ceramic with a low relative density of 76.5%, prepared at same SPS conditions [56], using 25 vol% SiC as reinforcement significantly affected the densification behavior, so that a composite with a relative density of 95.0% was obtained at 1850°C under 40 MPa for 6 minutes. Neck formation and well connection of grains in the microstructure (see Figure 1(a)) reveals that the SiC addition can promote the densification. Shahedi Asl et al. [61] reported a relative density of 93.9% for ZrB$_2$–25 vol% SiC composite, hot pressed at 1850°C under 20 MPa for 1 h. Hence, it is possible to achieve the same density in ZrB$_2$–SiC composites by applying a shorter time when the SPS route is used. Anyway, they reported a relative density of 99.3% for similar composite by hot pressing at an ultrahigh temperature of 2000°C [60]. As revealed in Figure 1(b), the introduction of g-C$_3$N$_4$ to the ZrB$_2$–SiC system has improved the densification and resulted in a porosity-free ZSC composite with a relative density of 100.8%. Such a weird result (RD >100%) might be attributed to the in-situ formation of new phases, such as ZrC with a higher theoretical density than those of the initial components, but it has been ignored in the reference density calculations. Anyway, the porosities have been removed from the microstructure, and the sintering has entirely progressed by the addition of 5 wt% C$_3$N$_4$ to ZrB$_2$–SiC composite.

The phase composition of the SPSed samples was identified by XRD analysis. The results of Rietveld refinement analysis, performed on the XRD patterns of ZS and ZSC samples, are presented in Figure 2. ZrB$_2$ and SiC were identified as the detected phases in the ZS ceramic (Figure 2(a)). Such an observation demonstrates that SiC does not react with ZrB$_2$ because it is a nonreactive reinforcement. In addition to ZrB$_2$ and SiC as the main phases, the introduction of C$_3$N$_4$ into ZrB$_2$–SiC composites resulted in the appearance of new compounds. As it can be seen in Figure 2(b), small peaks related to ZrC and BN phases are found in the XRD spectrum as the in-situ synthesized compounds. There is no trace of C$_3$N$_4$ in the XRD pattern of ZSC ceramic; therefore, it seems that C$_3$N$_4$ has completely consummed during the spark plasma sintering process. In-situ synthesized ZrC and BN, as the secondary phases, are formed due to the chemical reactions among the ZrB$_2$ particles and/or oxide impurities (ZrO$_2$ and B$_2$O$_3$) with the partial decomposition products of C$_3$N$_4$ additive (N$_2$ and C), according to the following equations:

$$C_3N_4 = 3C + 2N_2(g) \quad (3)$$

$$ZrB_2 + C + N_2(g) = ZrC + 2BN \quad (4)$$

$$B_2O_3 + 3C + N_2(g) = 2BN + 3CO(g) \quad (5)$$

$$ZrO_2 + 3C = ZrC + 2CO(g) \quad (6)$$

There is no available thermodynamics data in the database of HCSC Chemistry software for the C$_3$N$_4$, but it is reported that C$_3$N$_4$ completely decomposes to its constituent elements at temperatures above 750°C [63]. Hence, applying such a high sintering temperature of 1850°C certainly leads to the decomposition of C$_3$N$_4$ to carbon and nitrogen.

Figure 3 presents the standard Gibbs free energy variations versus temperature for the probable

![Figure 1](image1.png)

Figure 1. FE-SEM micrographs of the polished area of (a) ZS and (b) ZSC ceramics by backscattered electrons.
Figure 2. Rietveld refinement results (observed, simulated and difference) of SPSed samples: (a) ZS and (b) ZSC.
chemical reactions according to Eqs. 4–6. Due to the strongly negative Gibbs free energy of Eq. 4 at the room temperature up to the processing temperature of 1850°C (see Figure 3), this reaction is always thermodynamically desirable, and production of both BN and ZrC as the in-situ phases are feasible. Chemical reductions of surface oxides (Eqs. 5 and 6) have negative Gibbs free energy values above 1043°C and 1669°C, respectively. Such chemical reactions encourage the in-situ synthesis of the BN and ZrC phases, and improve the sinterability via increasing the contact between the oxide-depleted ZrB2 particles.

Rietveld refinement technique can be used to obtain the crystallographic information of the crystalline phases in ZS and ZSC samples quantitatively. A summary of these data is presented in Tables 2 and 3. Based on the results reported in these tables, SiC is a non-reactive component in both samples, because its amount has negligibly changed before and after the sintering process. Anyway, such differences not only can be attributed to the Rietveld refinement errors, but also to the removal of some oxides which led to the increase in the SiC content. Rietveld results for both composites show that the lattice parameters of the ZrB2, SiC, ZrC, and h-BN are in agreement with other reports [64–67].

Figure 4 shows the fracture surface of the ZSC composite, including the in-situ synthesized secondary phases. The layer-shaped phases are in harmony with the morphology of BN as an in-situ formed phase or C3N4 as an ex-situ introduced additive. Since no trace of carbon nitride was found by the XRD analysis, it seems that such phases can be related to the BN compound. Other non-layered interfacial phases may be attributed to the in-situ formed ZrC.

Mechanical properties of the as-prepared ZrB2-based materials (ZS and ZSC samples) are listed in Table 4. As a comparative purpose, the quantitative results of our previous study [56] are also included in this table. It should be noted that the codes of Z and ZC in Table 4 are representatives of the monolithic ZrB2 ceramic and the C3N4-doped ZrB2 sample, respectively. Adding 5 wt

![Figure 3. Gibbs free energy of chemical reactions of Eqs. 4–6 versus temperature.](image)

![Figure 4. SEM image of ZSC sample revealing the presence of in-situ phases.](image)

### Table 2. Quantitative analysis, crystallography data, and lattice parameters of ZS composite estimated through Rietveld refinement technique.

| Identified phases | Weight fraction (wt%) | Unit cell dimensions |
|-------------------|-----------------------|---------------------|
|                   | Before SPS | After SPS | | a = b (nm) | c (nm) | α = β | γ |
| ZrB2              | 85.12      | 82.16     | Hexagonal | P6/mmm | 0.316911 | 0.353154 | 90 | 120 |
| SiC               | 14.88      | 17.84     | Cubic     | F-43 m | 0.435913 | 0.435913 | 90 | 90 |

### Table 3. Quantitative analysis, crystallography data and lattice parameters of ZSC composite estimated through Rietveld refinement technique.

| Identified phases | Weight fraction (wt%) | Unit cell dimensions |
|-------------------|-----------------------|---------------------|
|                   | Before SPS | After SPS | | a = b (nm) | c (nm) | α = β | γ |
| ZrB2              | 81.64      | 78.96     | Hexagonal | P6/mmm | 0.316803 | 0.353050 | 90 | 120 |
| SiC               | 14.27      | 16.86     | Cubic     | F-43 m | 0.435910 | 0.435910 | 90 | 90 |
| C3N4              | 4.08       | 0         | Hexagonal |        | 0.467324 | 0.467324 |     |     |
| ZrC               | 0          | 2.17      | Cubic     |        | 0.250999 | 0.668999 | 90 | 120 |
| BN                | 0          | 2.16      | Hexagonal | P-3 m1 |        |        |     |     |
% C$_3$N$_4$ to ZrB$_2$–SiC ceramic composites resulted in an improvement in the hardness from 17.43 to 21.2 GPa. Relative density enhancement is one of the reasons for improving Vickers hardness, so that, the hardness has increased by about 22% with increasing the relative density from 95 to 100.8%. As it can be seen in Table 4, the hardness value is reported 10.1 GPa for the mono-lithic ZrB$_2$ [56], fabricated under similar sintering conditions, displaying the desirable effect of SiC on the hardening of ZrB$_2$-based ceramics. The addition of SiC could enhance the densification and decrease the porosity significantly; thus, the hardness enhancement not only might be related to the intrinsic higher hardness of SiC, but also to its constructive role in approaching the reference density. Using only 5 wt% C$_3$N$_4$ in the ZrB$_2$ matrix enhanced the hardness from 10.1 to 16.2 GPa, reported in our previous study [56]. In other words, hardness was greatly increased to 21.2 GPa, when SiC and C$_3$N$_4$ were simultaneously added into the ZrB$_2$. It should be noted that hardness of 14.6 GPa was obtained for ZrB$_2$-based ceramic, with a relative density of 98%, synergistically reinforced with SiC and Si$_3$N$_4$ [68]. Achieving high hardness (21.2 GPa) for the ZSC ceramic in the present research not only is attributed to its high relative density (100.8%), but also is a result of the in-situ formation of ZrC with an intrinsic higher hardness than those of ZrB$_2$ and SiC phases.

The values of fracture toughness of SPSed ZrB$_2$-based ceramic composites are also presented in Table 4. Compared to the estimated fracture toughness value of 3.8 MPa.m$^{1/2}$ for ZrB$_2$–SiC sample with an RD of 93.2% [69], the fracture toughness of the ZS sample (4.5 MPa.m$^{1/2}$) is considerable. A fracture toughness of 6.1 MPa.m$^{1/2}$ was attained for the fully dense ZSC specimen that is higher than that of the ZS sample (4.5 MPa.m$^{1/2}$) with a lower relative density of 95%. Using 5 wt% C$_3$N$_4$ in ZrB$_2$–SiC system not only encouraged the densification and increased the hardness, but also enhanced the fracture toughness.

SEM micrographs of the crack propagation paths in the polished surface of the as-sintered samples, caused by the Vickers indentation method, are demonstrated in Figure 5. There are several crack deflections as a main toughening mechanism in ceramic matrix composites, and breakage of large SiC grains in the ZS sample (Figures 4(a–b)) to Figures 5(a–b)). Interaction of crack with secondary phases (SiC in here) is usually known as the main reason for crack deflections. In addition to the number of crack deflection, its deviation angle also affects the energy absorption during the crack propagation [70–72]. Figure 5(c–d) displays how the cracks propagate and interact with the secondary phases, including SiC, BN, and ZrC. Several toughening mechanisms like crack deflection, breakage of SiC grains, crack branching, crack bridging, and microcracking are seen in Figure 5(c–d). It should be mentioned that toughening in ZSC composite can also be related to the layered structure of BN, with a high aspect ratio, and the formation of weaker interfacial bonding.

The values of flexural strength of ZS and ZSC, tested at room temperature, are presented in Table 4. Grain size, relative density, additive type as well as defects can affect the flexural strength of ceramic matrix composites. Hence, a wide range of flexural strength values from 275 to 630 MPa were reported for the monolithic ZrB$_2$ [73–75]. A flexural strength of 1060 MPa was gained for the hot-pressed ZrB$_2$–SiC composite, when the sample was manufactured using smaller ZrB$_2$ particles [76]. Compared to the additive-free ZS composite with a flexural strength of 460.2 MPa, C$_3$N$_4$ addition resulted in an improvement to 580.2 MPa. Enhanced densification and fine-grained microstructure can be supposed as essential factors on the composite strengthening. The SEM micrographs of the fracture surfaces are shown in Figure 6. As it can be observed in the microstructure of the ZS sample (in Figure 6(a)), the mean size of ZrB$_2$ grains (5.5 µm) is higher than the particle size of initial ZrB$_2$ powder (<2 µm). As shown in Table 4, the simultaneous addition of SiC and C$_3$N$_4$ was more effective in preventing extreme grain growth, as the mean grain size of ZrB$_2$ reduced from 5.5 to 3 µm when the C$_3$N$_4$ was added to the composite. It should be mentioned that the grain size of ZrB$_2$ in C$_3$N$_4$-doped ZrB$_2$ ceramic (ZC), reported in our previous work [56], was estimated 4.5 µm, smaller than that of the ZS sample. Such a result shows the importance of C$_3$N$_4$ in microstructural refinement and mechanical property improvement. A mixed intergranular/transgranular fracture mode is observed in the fracture surface of the ZS sample (Figure 6(a)). In contrast, intergranular breakage is identified as the dominant fracture mode in the fractograph of the ZSC specimen (Figure 6(b)). It seems that weak interfacial bonding between the

### Table 4. Properties of the spark plasma sintered ZrB$_2$-based composites.

| Sample code | Relative density (%) | Fracture toughness (MPa.m$^{1/2}$) | Vickers hardness (GPa) | Flexural strength (MPa) | Average Grain size of ZrB$_2$ (µm) | Note |
|-------------|----------------------|------------------------------------|------------------------|------------------------|------------------------------------|------|
| Z           | 76.5                 | 1.9 ± 0.2                          | 10.1 ± 1.6             | 187.6 ± 15             | 8                                  | Previous work [56] |
| ZS          | 95.0                 | 4.5 ± 0.3                          | 17.4 ± 2.3             | 460.2 ± 20             | 5.5                                | Present work |
| ZC          | 99.8                 | 5.4 ± 0.4                          | 16.2 ± 2.2             | 516.4 ± 20             | 4.5                                | Previous work [56] |
| ZSC         | 100.8                | 6.1 ± 0.4                          | 21.2 ± 2.5             | 580.2 ± 25             | 3                                  | Present work |

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particles, because of the formation of soft-layered BN in the as-SPSed composite, is the main reason for this phenomenon.

4. Conclusions
ZrB$_2$–25 vol% SiC ceramic composites, with and without g-C$_3$N$_4$ sintering aid, were spark plasma sintered at 1850°C for 6 min under 40 MPa. The addition of g-C$_3$N$_4$ into ZrB$_2$–SiC composite was found as a favorable way to promote the sinterability and mechanical feathers (flexural strength, Vickers hardness, and indentation fracture toughness) of ZrB$_2$-based composites. The introduction of C$_3$N$_4$ increased the relative density from 95 to 100.8%. Elimination of oxide contaminations (ZrO$_2$ and B$_2$O$_3$) from the surface of ZrB$_2$ particles, as a result of C$_3$N$_4$
addition, led to the in-situ synthesis of BN and ZrC compounds. A fracture toughness of 6.1 MPa.m$^{1/2}$, a flexural strength of 580.2 MPa, and a Vickers hardness of 21.2 GPa were attained for the C$_3$N$_4$-doped ZrB$_2$–SiC composite.

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