Role of Si₃N₄ on microstructure and hardness of hot-pressed ZrB₂−SiC composites

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A B S T R A C T

The impact of Si₃N₄ content on the hardness and microstructural developments of ZrB₂-SiC material has been investigated thoroughly in the present investigation. Having prepared the raw materials in a jar mill, the ZrB₂-SiC samples containing various amounts of Si₃N₄ were hot-pressed at 1850 °C. Furthermore, XRD, FESEM, and HRTEM were utilized to evaluate the microstructure of samples. The formation of in-situ h-BN was proved by the mentioned methods. Also, it was shown that the Vickers hardness of ZrB₂-SiC increases up to 20 GPa in presence of 4.5 wt% Si₃N₄ which is 3 GPa more than the sample without Si₃N₄. Results show that the positive effect of increased relative density on hardness is more than the negative effect of h-BN soft phase formation.

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1. Introduction

Nowadays, ultra-high temperature ceramics (UHTCs) are used in the cutting-edge technological progresses. ZrB₂ with the hexagonal structure is one of the most applicable UHTCs. ZrB₂ has suitable thermal and mechanical properties, high temperature resistance, high corrosion resistance, and high melting point, which make it a suitable material to be used in high temperature structural applications, e.g., space crafts. Despite all these marvelous properties, ZrB₂ cannot be easily sintered. Furthermore, it is fragile and does not have a good anti-oxidation property. A practical method for solving these problems, which limit the application of ZrB₂, is composing it with other ceramics or metals [1–5].

The most important ZrB₂-based composite is ZrB₂−SiC, which is usually produced by various sintering procedures, i.e., pressure-less sintering, hot-pressing, microwave sintering and so on. SiC improves the sinterability of composite by reducing the surface oxides of ZrB₂. SiC also inhibits the grain growth. Nano-SiC particles not only give the composite more anti-oxidation resistance, but they also create a composite with high bending strength. Although making composite with SiC reduces the limitations of ZrB₂, using dopants in the composite may enhance the mechanical properties in a way that the final product will be even much more applicable [6–9]. There is a huge body of literature studied the microstructure and mechanical features of ZrB₂−SiC in presence of various additives. Si₃N₄ is one of the additives which has the most impact on the structural properties of ZrB₂−SiC composite. By the way, the exact impacts of Si₃N₄ on various characteristics of hot-pressed ZrB₂−SiC materials have not been investigated thoroughly [10,11]. Liu et al. [12] investigated the improved mechanical properties of laminated ZrB₂−SiC composites with interfacial porous Si₃N₄. They
proposed that the notable high-temperature strength of final product may be attributed to the porous Si₃N₄ whisker which absorbs the glassy phase gathered at the crack tip, avoiding grain boundary sliding. Golla et al. [13] studied the oxidation and microstructure behavior of ZrB₂-20 vol% SiC composites introduced by Si₃N₄ and Ta additives using spark plasma sintering at 1900 °C. They concluded that the microstructure of composite is comprised of new secondary phases (BN, ZrN, ZrO₂), together with ZrB₂ and SiC. They also showed that Ta improves the oxidation properties more than Si₃N₄. In another investigation accomplished by Thimmappa et al. [14], oxidation behavior, hardness, and phase stability of SPSed ZrB₂-SiC-Si₃N₄ materials were studied. ZrB₂-20 vol%-SiC-5vol% Si₃N₄ hardness was determined to be 30.56 GPa. Ahmadi et al. [15] examined the Sintering behavior of ZrB₂–SiC composites doped with Si₃N₄. They showed that relative density increases by the incorporation of Si₃N₄ in hot-pressed specimens. A reverse trend was observed in pressureless sintered composites, owing to the generation of gaseous byproducts, resulting in the entrapment of more pores in the ultimate structure. Zou et al. [16] studied mechanical properties of ZrB₂-20 vol% SiC materials. They evaluated strength on the basis of temperature in terms of the grain sizes, microstructural defects, differences in oxygen content, grain boundary phases, and nature of fracture. Pourmohammadie Vafa et al. [17] investigated graphite introduction on the properties of as-sintered ZrB₂–SiC ceramics. Phase analysis of hot-pressed specimens showed the generation of the in-situ B₄C and Zr₃C₂ phases, along with the original compounds. Shahedi Asl et al. [18] investigated the microstructure of SPSed ZrB₂–based composites introduced by nano-sized SiC dopants using TEM technique. TEM studies confirmed the generation of such phases, which were comprised of a Si–B–O glassy bed with C and ZrC islands distributed therein. Although some brilliant researches have been carried out on the characteristics of ZrB₂–SiC-Si₃N₄ composites, in this work we have tried to study the microstructure of such composites using polished and fractured surfaces, as well as prepared FIB samples. Moreover, the impact of various Si₃N₄ content on the hardness and sinterability of ZrB₂-SiC has been investigated, too. For this objective, after the preparation of raw materials and hot-pressing process, density and hardness of samples were calculated. Furthermore, XRD, FESEM, and HRTEM were utilized for evaluating the microstructures. The aim of this investigation is to study the structural changes caused by Si₃N₄ in the ZrB₂-SiC composite, which lead to higher hardness values.

2. Experimental procedure

2.1. Starting materials and fabrication method

The raw powders of Si₃N₄, SiC, ZrB₂, and phenolic resin (5 wt%) were employed in this examination as the raw materials. Table 1 provides some useful information associated with these materials. To assess the impact of Si₃N₄ content on the microstructure, sintering behavior, and mechanical characteristics of ZrB₂-SiC substances, four different samples were designed to be fabricated (Table 2). For doing so, at first, the required ingredients for each designed specimen were weighed precisely, and then, were dispersed using a jar-mill facility (ZrO₂ balls and Teflon cup) in the ethanol medium. Subsequently, a rotary evaporation device was used to remove the ethanol medium at 100 °C. Uniform admixtures were secured by grinding the dried slurries and passing them through a 100-mesh screen. Finally, the prepared mixtures were hot-pressed under 20 MPa at 1850 °C for 90 min.

2.2. Characterization

The relative density values of samples were reported as the proportions of bulk and theoretical densities. The crystalline phases of each composite were examined using an XRD device (PW1800, Philips). Moreover, both fracture and polished surfaces of samples were studied in terms of microstructures, by a FESEM (Mira3, Tescan), coupled with an EDS analyzer. Moreover, a complementary microstructural examination was accomplished by an HRTEM (F20 S-TWIN, Philips). The HSC chemical package was utilized to check the feasibility of the probable chemical reactions over the hot-pressing process. Vickers technique was employed to determine the hardness of hot-pressed samples by exerting 49 N load on the polished surfaces for 14 s. For each specimen, at least six indentations were carried out.

3. Results and discussion

Based on the XRD spectra and FESEM images of as-received ZrB₂, SiC, and Si₃N₄ powders (not shown here), the shape of SiC particles is polyhedral. SiC particles are not agglomerated and they are in the range of 3-10 µm. The size of agglomerated Si₃N₄ is about 1-3 µm. Finally, the size of ZrB₂ is smaller than 5 µm. Powders with different sizes could break down and be put together in a pack during the pressing. In this case, the final product could be close pack and the density of composites will be enhanced. ZrB₂, SiC and Si₃N₄ have hexagonal structures. Furthermore, the XRD patterns of powders roughly show the single-phase high-purity products. Only a single peak for SiO₂ could be detected in the SiC pattern, which could be attributed to the surface oxidation. According to references, there have to be other oxides like B₂O₃ and ZrO₂ on the surface of ZrB₂ [19–25]. The reason for existence of these oxides is due to high oxidation tendency of carbides, borides and nitrides on the surface to be thermodynamically stable [26,27]. Since the amounts of such oxides are less than other phases (usually under 2.5%), they usually cannot be identified by XRD.
Fig. 1 illustrates the relative density of ZrB$_2$-SiC composites containing various amounts of Si$_3$N$_4$. As it is illustrated, the relative density of HPed composites is enhanced by increasing the amount of Si$_3$N$_4$. The relative density of ZrB$_2$-SiC composite is about 91.4% after sintering, which reaches 99.3% for the sample containing 4.5 wt% Si$_3$N$_4$. The enhanced relative density may enhance the mechanical properties of the final sample. Porosities are the preferred locations for crack propagations, which could reduce the strength and hardness of ceramics. A probable reason for increasing the relative density of ZrB$_2$-SiC system in the presence of Si$_3$N$_4$ additive could be the in-situ generation of some phases that could help the sintering process. A thermodynamic investigation of probable chemical reactions is needed for a better understanding of this phenomenon.

Fig. 2 indicates the XRD patterns of the hot-pressed ceramics containing 3 and 4.5 wt% Si$_3$N$_4$. As is indicated, hexagonal ZrB$_2$ (Reference code: 00-034-0423), SiC (Reference code: 00-031-1232) and BN (Reference code: 01-085-1068) are detected in these patterns. The amount of BN phase is increased by enhancement of the Si$_3$N$_4$ content in the sample, which is recognized by the relative intensity of XRD peaks. The only variable among samples is the addition of various amounts of Si$_3$N$_4$. Therefore, there have to be some chemical reactions between Si$_3$N$_4$ and other starting materials for the formation of BN phase.

According to the previously published papers, surfaces of as-received powders, i.e., ZrB$_2$ and SiC, contain surface oxides, such as SiO$_2$, B$_2$O$_3$, and ZrO$_2$. In fact, the initial admixture is comprised of ZrB$_2$, SiC, and Si$_3$N$_4$ original phases and the surface oxides of SiO$_2$, B$_2$O$_3$ and ZrO$_2$. Several chemical interactions may be related to these existing materials which are introduced in Fig. 3.

Fig. 3 shows the Gibbs free energy vs. temperature for the possible chemical reactions in this system. These reactions can take place in the standard pressure of 1 atm; so, in hot-pressing process these reactions may happen in lower temperatures, due to higher applied pressure. The most negative value of Gibbs free energy is for the reaction between Si$_3$N$_4$ and B$_2$O$_3$ as it is illustrated in Eq. (1).

$$\text{Si}_3\text{N}_4 + 2\text{B}_2\text{O}_3 \rightarrow 4\text{BN} + 3\text{SiO}_2$$  \hspace{1cm} (1)

According to Eq. (1), BN can be generated in the interface of ZrB$_2$/Si$_3$N$_4$, because B$_2$O$_3$ oxide is available on the surface of ZrB$_2$ [19–25]. As is illustrated in Fig. 3, within the whole temperature range, the Gibbs free energy of Eq. (1) is the lowest amongst all possible reactions; accordingly, the mentioned reaction occurs while the reactants exist. There is also another reaction between Si$_3$N$_4$ and B$_2$O$_3$ (Eq. (2)), which could progress above 1600 °C by turning the Gibbs free energy towards negative values.

$$\text{Si}_3\text{N}_4 + \text{B}_2\text{O}_3 \rightarrow 2\text{BN} + 3\text{SiO(g)} + \text{N}_2(g)$$  \hspace{1cm} (2)

If there is an adequate amount of reactants, Eq. (2) is the second possible equation in this system. Si$_3$N$_4$ reacts with SiO$_2$ to form gaseous SiO and N$_2$ as well as liquid Si as shown in Eq. (3).

$$\text{Si}_3\text{N}_4 + \text{SiO}_2 \rightarrow 2\text{SiO(g)} + 2\text{Si(l)} + 2\text{N}_2(g)$$  \hspace{1cm} (3)

Eq. (3) has a negative Gibbs free energy value above 1700 °C. Therefore, this equation could be the third possible reaction happening in this system. Liquid Si could be helpful in sintering process and a scientific reason for higher relative densities of samples containing...
\[ \text{Si}_3\text{N}_4 + 3\text{C} = \text{SiC} + 2\text{N}_2(g) \]  

According to Eq. (5), Si$_3$N$_4$ is one of the reactants; therefore, the amount of Si$_3$N$_4$ in situ-formed BN will increase by introducing more Si$_3$N$_4$ in the composite. This can be concluded from the intensity of BN main peaks of the XRD patterns. As it was noted previously, the only limit for formation of BN is the existence of reactants; therefore, the amount of in-situ formed BN will be increased by incorporating more Si$_3$N$_4$. There should also be some amount of carbon extracted from pyrolyzed resin among reactants. Carbon could react with some ingredients and form other in-situ phases. There are two possible reactions between Si$_3$N$_4$ and carbon. Eq. (7) shows the reaction amongst Si$_3$N$_4$, carbon and ZrB$_2$, producing two carbides, a nitride and gaseous nitrogen.

\[ 4\text{C} + \text{Si}_3\text{N}_4 + \text{ZrB}_2 = \text{ZrC} + 2\text{BN} + 3\text{SiC} + \text{N}_2(g) \]  

According to [19], Eq. (7) could be feasible above 975 °C. Accordingly, Eq. (7) would be the second chief reaction in this system if enough content of carbon were present. Eq. (7) also relies upon the amount of Si$_3$N$_4$ and it would be more favorable with higher Si$_3$N$_4$ content. Si$_3$N$_4$ additive can also interact with carbon and form N$_2$ and SiC via Eq. (8).

\[ \text{Si}_3\text{N}_4 + 3\text{C} = 3\text{SiC} + 2\text{N}_2(g) \]  

Eq. (8) is possible at temperatures over 1450 °C, based on the Gibbs free energy values. The remaining carbon could remove oxides from the surface of particles. The existence of oxide phases on the surface of initial particles could be a detrimental factor on grain coarsening over sintering process. Residual carbon can individually reduce oxide impurities, based on the following reactions.

\[ \text{ZrO}_2 + \text{B}_2\text{O}_3(l) + 5\text{C} = \text{ZrB}_2 + 5\text{CO}(g) \]  

\[ \text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}(g) \]  

\[ \text{ZrO}_2 + 3\text{C} = \text{ZrC} + 2\text{CO}(g) \]  

These reactions are possible at temperatures higher than 1500 °C. The products of Eq. (9) to Eq. (11) may improve the sinterability of ZrB$_2$–SiC ceramics. These reactions were also reported in some other researches [19,31,32], but it should be considered that the amount of remaining carbon may be diminished, thanks to the progression of several abovementioned reactions. Hence, the advancement of such reactions may be limited by lack of carbon. It was reported that the generation of interfacial fine ZrC ingredient may enhance the sinterability of ZrB$_2$-based materials [28–30], though it sounds that the resulted CO can impair the densification stage. According to the above discussion it could be concluded that Eq. (1) can be the main reaction in this system, leading to the in-situ formation of BN. Other reactions may be limited due to the shortage of Si$_3$N$_4$ and carbon content. However, small amounts of other in-situ products could be formed during hot-pressing, too. Based on our sight of view, and upon the results of XRD (Fig. 2), the main available phases in the final composites are ZrB$_2$ and SiC, as well as the in-situ produced BN, which should be studied more by FESEM and HRTEM techniques. Fig. 4 shows the backscattered FESEM images of the polished ZrB$_2$–SiC composites containing various amounts of Si$_3$N$_4$. As is shown, the remaining pores are detectable in S0, S1.5 and even S3 samples. As was mentioned previously, during sintering process and by increasing the amount of Si$_3$N$_4$, liquid Si will form according to Eq. (3) and (5). This liquid phase could remove the porosities and help the composites to be more compact. Furthermore, the existence of Si$_3$N$_4$ can trigger some chemical reactions, improving densification.

Fig. 5 shows the backscattered FESEM image of the polished surface of ZrB$_2$–SiC ceramic containing 4.5 wt% Si$_3$N$_4$ additive. A smooth surface without any apparent porosity can be seen in this image. EDS maps show that C, N, O and B are uniformly distributed on the polished surface. As it was mentioned earlier, BN phase is formed in the interfacial area of ZrB$_2$ and Si$_3$N$_4$ particles. Therefore, for the evaluation and illustration of BN, higher magnification is needed.
Fig. 6 shows the backscattered fractograph of S3 sample. As is indicated, the S3 sample is mainly comprised of ZrB₂ and SiC phases, in which some in-situ h-BN compound is formed. In other words, by introducing Si₃N₄ to the composite samples, the BN phase initiates to nucleate on the surface of ZrB₂ where Si₃N₄ particles exist.

Fig. 7 illustrates the HRTEM images of the S4.5 sample. Two different interfaces of SiC and ZrB₂ have been shown in these images. Fig. 7(a) shows an interface between ZrB₂ and SiC phases. As is shown, there is not any BN or other synthesized phases formed in this interface. This interface has been marked as clean interface. Fig. 7(b) shows an interface between SiC and ZrB₂ with BN phase between them. It seems that, Si₃N₄ particles convert into BN phase. According to thermodynamic investigations, it seems that the nucleation of BN phase initiates between Si₃N₄ and B₂O₃ on the surface of ZrB₂.

One of the problems associated with composite materials is the weak mechanical junctions in the interfacial areas. Although sintering process helps the diffusion bonding and also promotes chemical reactions at interfaces, these areas mostly have a detrimental impact on mechanical properties. The mentioned h-BN phase synthesized in-situ between SiC and ZrB₂ particles, could even increase this detrimental impact due to its soft nature.

Fig. 8 plots the Vickers hardness values of S0, S1.5, S3 and S4.5 samples. The curve illustrates hardness as a function of Si₃N₄ content. As is clear, the Si₃N₄ incorporation has generally a positive impact on the hardness of specimens. The hardness value for S0 sample is about 17 GPa; however, the S1.5 sample experiences a slight reduction by the addition of 1.5 wt% Si₃N₄. By contrast, the samples get harder by adding more Si₃N₄ content. The most significant Vickers hardness is related to S4.5 sample, standing at 20 GPa.

As was mentioned earlier, there are two main factors affecting hardness of this composite system, i.e., the improvement of relative density, which has a positive effect and the formation of h-BN, which has a negative effect. It seems that for the S1.5 sample, the effect of h-BN formation is dominant over the enhancement of relative density. However, for the S3 and S4.5 samples, increasing relative density is dominant over the formation of h-BN phase, leading to higher values of Vickers hardness.
4. Conclusion

The impact of Si$_3$N$_4$ content on the hardness and microstructural development of Zrb$_2$-SiC material has been investigated thoroughly in the present investigation. The following results are the main conclusions of this investigation:
- BN phase forms in the interface between SiC and Zrb$_2$ phases by a reaction between B$_2$O$_3$ and Si$_3$N$_4$ ingredients.
- The amount of in-situ formed BN will increase by introducing more Si$_3$N$_4$.
- Although h-BN is a soft phase, the formation of it in the interface of Zrb$_2$-SiC composite not only did not decrease the hardness, but also improved this property thanks to the increased relative density.
- The Vickers hardness of Zrb$_2$-SiC ceramic is about 17 GPa, which increases up to 20 GPa by the addition of 4.5 wt% Si$_3$N$_4$.

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