Influences of $B_4C$ content and particle size on the mechanical properties of hot pressed TiB$_2$–B$_4$C composites

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ABSTRACT

TiB$_2$ ceramic has attracted many attentions due to its excellent performances both on mechanical and functional properties. However, it is still very difficult to obtain TiB$_2$ bulks with full densification. Herein, TiB$_2$–B$_4$C composites were prepared via hot pressing at 1900°C under the pressure of 35 MPa with TiB$_2$ and B$_4$C as the raw materials. The influences of B$_4$C content (0, 10 vol%, 20 vol% and 30 vol%) and particle size (0.50 µm, 3.12 µm and 7.09 µm) on the phase composition, relative density, microstructure and mechanical properties of TiB$_2$–B$_4$C composites were investigated. The using of 0.50 µm B$_4$C brought more B$_2$O$_3$ which induced oriented growth of TiB$_2$ grains and coarsened the obtained composites. When the raw B$_4$C powders were 3.12 µm and 7.09 µm, the obtained composites with 20–30 vol% B$_4$C could be fully densified. TiB$_2$–30 vol% B$_4$C composite prepared from 3.12 µm B$_4$C powder resulted in the optimal mechanical properties. The bending strength, Vickers hardness, fracture toughness were 671 MPa, 27.93 GPa, and 3.91 MPa$^{-1/2}$, respectively. The excellent performance was attributed to its fine and homogenous microstructure.

1. Introduction

Titanium diboride (TiB$_2$) is a high temperature resistant ceramic material, with exceptional hardness, high melting point, good chemical stability, excellent electrical and thermal conductivity [1–4]. These properties make TiB$_2$ be applied in many industries, such as wear resistant devices, protective materials, ultra-high temperature refractory. However, due to its low self-diffusion coefficient, monolithic TiB$_2$ ceramic exhibits a poor sintering property. The sintering temperature of monolithic TiB$_2$ ceramics is usually above 2000°C. High temperature sintering causes grain coarsening of TiB$_2$ and residual porosity, resulting in a low relative density. Therefore, monolithic TiB$_2$ ceramics show unsatisfied mechanical properties and poor oxidation resistance.

Fortunately, these drawbacks can be avoided by introducing the second phase. Many literatures have reported that the addition of second phases, including SiC, Si$_3$N$_4$, AlN, BN, TiN, TiC, TiSi$_2$ and Ti$_3$AlC$_2$, etc., greatly improves the sintering performance of TiB$_2$, and the formed TiB$_2$-based ceramics exhibit excellent properties [1–8]. Among various second phase additives, B$_4$C is particularly noteworthy and TiB$_2$–B$_4$C has the potential to become one of the most attractive TiB$_2$-based composites owing to the following reasons. Firstly, no chemical reaction occurs between TiB$_2$ and B$_4$C, indicating a good chemical compatibility, which makes them easy to form composites. Secondary, similar to TiB$_2$, B$_4$C also has high melting point, the formed TiB$_2$–B$_4$C composites can retain the high temperature properties of TiB$_2$. Thirdly, B$_4$C is a refractory material with ultrahigh hardness, the addition of B$_4$C into TiB$_2$ matrix will enhance the hardness and impact resistance of the material. Moreover, the mismatch of thermal expansion coefficient between TiB$_2$ and B$_4$C creates microcracks during the cooling process, which will consume the energy for the crack propagation and improve the toughness of the ceramic. In addition, B$_4$C can remove oxide from the TiB$_2$–B$_4$C system by the chemical reaction between B$_4$C and TiO$_2$. During the sintering process, oxygen has been proved to prevent densification of TiB$_2$ by promoting surface diffusion. As stated above, B$_4$C is effective to improve sinterability and mechanical properties of TiB$_2$ simultaneously.

Normally, in the dual phase system of TiB$_2$ and B$_4$C, TiB$_2$ is served as reinforcement for B$_4$C matrix and B$_4$C–TiB$_2$ composites are widely studied [9–14]. Recently, our group reported the effects of B$_4$C particle size on the microstructure and mechanical properties of hot-pressed B$_4$C–TiB$_2$ composites [15]. When the particle size of raw B$_4$C powder was coarse (above 3.0 µm), TiB$_2$ grain oriented with its [001] axis parallel to the
applied pressure direction due to its hexagonal crystal structure. However, when B₄C powder was only 0.5 μm, fine B₄C particles surrounded TiB₂ particles and hindered the orientation of TiB₂ grains. The starting B₄C particle size had little effect on the mechanical properties of the composites.

There are also some reports concern TiB₂–B₄C composites in which TiB₂ is the matrix while B₄C is the reinforced phase, but metal Fe or Ni is always used as a sintering aid [16–21]. The low melting point of metal Fe or Ni induces liquid sintering which improves densification, room flexural strength and fracture toughness but is unfavorable for hardness and high temperature properties. Huang et al. [22] fabricated TiB₂–B₄C composites by pulsed electric current sintering without using any additives, and the effects of B₄C content on the densification, microstructure and mechanical properties of the composites were investigated. The addition of 20 vol% or more B₄C not only made TiB₂–B₄C composites be nearly full densified but also improved the hardness and flexural strength.

In the present study, influences of B₄C content and particle size on the mechanical properties of hot pressed TiB₂–B₄C composites are discussed. The results will show that the optimum mechanical properties of TiB₂–B₄C composites requires appropriate B₄C content and particle size.

2. Materials and methods

The starting powders consisted of TiB₂ (Shanghai Naion Nano Technology Co., Ltd., Shanghai, China) and B₄C (Suzhou Nanopure Materials Technology Co., Ltd., Suzhou, China). The d₅₀ of TiB₂ powder was about 1.50 μm. In order to investigate the influence of B₄C particle size, B₄C powder with a d₅₀ of 7.09 μm, 3.12 μm and 0.50 μm were used, respectively. The TiB₂ and B₄C mixture powders were ball-milled at room temperature in ethanol for 12 h using ZrO₂ as the ball media. After mixing, the slurries were dried in the rotary evaporator at 70°C. Then the mixed powders were put into the vacuum drying oven at 90°C for 24 h.

In order to minimize mixed powders segregation and agglomeration, the completely dry powders were sieved with a 200-mesh sieve. Finally, these dried TiB₂–B₄C powders were filled into a graphite die, followed by HP fabrication in a hot press furnace (ZT-50-22Y, Shanghai Chen Hua Electric Furnace Co. Ltd., Shanghai, China) for 1 h at 1900°C under 35 MPa. After heat preservation, the pressure was gradually removed and the whole system was cooled down naturally to indoor temperature. To investigate the influence of B₄C content, the fraction volume of B₄C was selected as 10, 20, 30 vol%, respectively. Their nomenclatures are T10B, T20B, T30B in turn.

The sintered samples were ground by a grinder to remove the graphite foil and surface layer, and then processed by wire cut electrical discharge machining (WEDM) with a test size of 1.5 mm × 2.0 mm × 25 mm (thickness, width and length, respectively). The density values of the TiB₂–B₄C composites were measured based on the standard Archimedes method. The phase components and microstructures of specimens were characterized by X-ray diffraction (XRD, Ultima IV, Rigaku Co, Japan) and scanning electron microscopy (SEM, JSM-6510LV, JEOL, Japan), respectively. The Vickers hardness (Hᵥ) was measured using a hardness tester (HMV-2T, Shimadzu Corporation, Kyoto, Japan), and the load was 19.6 N for 10 s. The fracture toughness was calculated by the indentation fracture method according to Equation (1) [23]:

\[ K_C = 0.16H/V(a)^{2.5} \]  

(1)

where Kᵥ is the fracture toughness, Hᵥ is the hardness, a is the impression radius and C is the indentation crack length. The bending strength was determined by the three-point bending method using an electromechanical universal testing machine (Exceed E44, MTS China, Shenzhen, China). The bending load was applied with a load speed of 0.1 mm/min and a span of 20 mm, and parallel to the hot-pressing axis. The values were calculated based on the average of 10 indentations for Vickers hardness and fracture toughness. The values of bending strength for each sample were calculated from the best 5 values according to the performance of at least 8 bars.

3. Results and discussion

The XRD patterns of TiB₂–B₄C composites with different B₄C contents and particle sizes are shown in Figure 1. The measured surface is perpendicular to the hot pressing direction. It is obvious that the phase constituents of all composites are TiB₂ and B₄C, and no other impurity phase phases are detected. The results indicate that TiB₂ and B₄C do not react during the sintering process and have a good high temperature compatibility. For monolithic TiB₂ ceramics, the diffraction intensity of (001) is higher than that of (100), indicating that TiB₂ grains have a preferential orientation growth with the [001] direction parallel to the mechanical field during the sintering process. The addition of B₄C powders with different contents and particle sizes show different influences on the oriented growth of TiB₂ grains. When the raw B₄C powders is 0.5 μm, the presence of B₄C greatly prevent the orientation of the TiB₂ grains in TiB₂–B₄C composites. As shown in Figure 1(a), when the B₄C content is 10–20 vol%, the diffraction intensity of (100) plane for the TiB₂ phase in the composite is higher than that of (001), which is consistent with that of the standard TiB₂ phase (JCPDS card 35–0741). However, the intensity ratio of I(001)/I(100) for the TiB₂ phase in the composite
Figure 1. XRD patterns of TiB$_2$–B$_4$C composites with different B$_4$C contents using (a) 0.50 µm and (b) 3.12 µm B$_4$C. (c) XRD patterns of TiB$_2$–30 vol% B$_4$C composites using B$_4$C powders with different particle sizes.

is still higher than that of standard phase, indicating that there is still some oriented TiB$_2$ grains in the composites. When the B$_4$C content reaches 30 vol%, the diffraction intensity of (001) for the TiB$_2$ phase is enhanced to higher than that of (100), reflecting improved orientation. When the raw B$_4$C powders is 3.12 µm (Figure 1(b)), with increasing B$_4$C content, the diffraction intensity of (100) plane slightly increases while that of (001) decreases. The above results mean that the addition of 3.12 µm B$_4$C gradually hinder the TiB$_2$ orientation during the sintering process. When the B$_4$C content is fixed at 30 vol% (Figure 1(c)), the intensity ratio of $I_{(001)}/I_{(100)}$ for the TiB$_2$ phase decrease with increasing B$_4$C particle size. Similar phenomena have been reported in our previous research [13].

The preferential orientation growth of the grains is related to three factors: the anisotropic crystal structure, the stress field, and the suitable growth environment. TiB$_2$ has a hexagonal crystal structure and tends to grow into plates or columns [24]. Previous report on the hot pressed TiB$_2$ has indicated that TiB$_2$ grains with a certain orientation tended to grow during sintering at the cost of grains that have a less favorable orientation, and the growth of the grains with the closely packed atomic layers perpendicular to the stress axis is energetically favorable [24]. The present of liquid or gas phase could accelerate the oriented growth of TiB$_2$ grains by dissolution, precipitation, and Ostwald ripening mechanism [25,26]. In the present study, B$_2$O$_3$ became liquid or gas phase at high temperature, which was produced by the self-oxidation of the raw TiB$_2$ and B$_4$C powders, as well as the reaction between TiO$_2$ (oxidation product of TiB$_2$) and B$_4$C during the sintering process. The addition of B$_4$C into TiB$_2$ hindered the grain growth of TiB$_2$ on the one hand but sometimes provided more liquid or gas B$_2$O$_3$ phase on the other hand. Therefore, the orientation growth of TiB$_2$ was affected by the above two factors, and the orientation degree depended on which factor was dominated.

When the raw B$_4$C powders is 0.5 µm, the influence of second phase (10–20 vol% B$_4$C) is dominant. Therefore, the intensity ratio of $I_{(001)}/I_{(1100)}$ for the TiB$_2$ phase in the composite decreases with increasing B$_4$C content. However, when B$_4$C reaches 30 vol%, the influence of liquid and gas phase plays a dominant position, resulting in the enhancement of $I_{(001)}/I_{(1100)}$, as shown in Figure 1(a). When the particle size of B$_4$C powders is 3.12 µm and 7.09 µm, the influence of the second phase is always dominant. As we know, the
oxidation behavior of the particle surface is closely related to its own size. When the raw $B_4C$ powders is 0.5 µm, the surface is more susceptible oxidized and produced more $B_2O_3$. When increasing particle size of $B_4C$, its surface is not easy to be oxidized and resulting in less $B_2O_3$. Correspondingly, the influence of the liquid phase is not enough to change the effect of the secondary phase, which could explain the declining of $I_{(100)}/I_{(110)}$ with increasing $B_4C$ particle size, as shown in Figure 1(c).

Figure 2 shows the relative densities of as-prepared TiB$_2$–$B_4C$ composites. With $B_4C$ addition, the relative densities of TiB$_2$–$B_4C$ composites are much higher than that of single-phase TiB$_2$ ceramics, indicating that $B_4C$ addition to the TiB$_2$ matrix significantly improves its relative density. When the raw $B_4C$ powders is 0.5 µm, as the $B_4C$ content increases, the relative density of the composite first increases to the maximum value of 97.2% and then decreases, which is consistent with previous analysis on the XRD patterns (Figure 1). The addition of secondary phase on the TiB$_2$ matrix improve the density of the composite by pinning effect, but too much $B_4C$ introduce more $B_2O_3$ which retarded the densification by the oriented growth of TiB$_2$. When the raw $B_4C$ powders is 3.12 µm, the relative density increased with increasing $B_4C$ content. When the $B_4C$ content is 10 vol%, the relative density of the TiB$_2$–$B_4C$ composite achieves 99.6%, indicating almost complete densification of the composite. As the $B_4C$ content continued to increase, the obtained composites are fully densified. When the raw $B_4C$ powders is 7.09 µm, the relative density also increased with increasing $B_4C$ content and reaches 100% at 30 vol% $B_4C$. It is clear that the relative density of composite prepared from 3.12 µm $B_4C$ powders is lower than that of the corresponding composite prepared from 3.12 µm $B_4C$ powders, which is attributed to the better pinning effect of second phase with smaller particle size on the matrix grains. The above results indicate that both the particle size and the content of the raw $B_4C$ powders affected the densification of the composite. When the $B_4C$ powder is submicron, the densification of the composite is more affected by the more $B_2O_3$ than by the pinning effect of finer particle size. However, when the $B_4C$ particle size is micron, both the smaller particle and the higher content favored the densification of the composite.

Figure 3 shows the backscattered electron (BSE) images of the polished surfaces of TiB$_2$–$B_4C$ composites. The bright phase is TiB$_2$ phase, whereas the dark phase is $B_4C$ phase. With 20 vol% $B_4C$ content, the microstructure of the obtained TiB$_2$–$B_4C$ composite becomes coarser with increasing particle size of raw $B_4C$ powder, indicating better pinning effect of smaller secondary phase on the matrix. However, when the $B_4C$ content is 30 vol%, although the used raw $B_4C$ powder is much finer, the grain sizes of both $B_4C$ and TiB$_2$ phases in Figure 3(b) are bigger than those in Figure 3(d). The result is accord to the previous analysis. Submicron $B_4C$ raw powder induced more $B_2O_3$ than micron powder. During the high temperature sintering process, the presence of $B_2O_3$ accelerated grain growth for both phase in the composite and resulted in the orientation of TiB$_2$ grains (Figure 1(c)). According to Figure 2 and Figure 3, it can be found that the TiB$_2$–$B_4C$ composite obtained from 3.12 µm $B_4C$ powders has the finest microstructure and the most uniform phase distribution with full densification. According to Figure 3, it seems that there has three different phases, which was analyzed by EDS, as shown in Figure 4. It was found that small amount of Zr presented in the diboride matrix, indicating the formation of solid solution of (Ti,Zr)B$_2$, which might be from the Zr impurity in the raw TiB$_2$ powder. Similar phenomenon was also reported in the $B_4C$–TiB$_2$ composites prepared from reactive sintering of elemental Ti, B and C [12].

To better analyze the microstructure and fracture mode of TiB$_2$–$B_4C$ composites, the SEI and BSE images of the fractured surface of TiB$_2$–30 vol% $B_4C$ composites prepared from $B_4C$ powders with different particle size are shown in Figure 5, respectively. The microstructures reflected in Figure 5 is consistent with those in Figure 3. From Figure 5(a) and (b), it is clearly seen that the fracture surfaces of large $B_4C$ grains are smooth and flat, indicating obvious intergranular fracture mode. The fracture surfaces of TiB$_2$ grains are uneven and have many edges and corners, which reveal that the fracture mode for TiB$_2$ grains is mainly intergranular. It should be noticed that there are many holes pitted in the large TiB$_2$ grains, as indicated in Figure 5(b) and Figure 5(d). Considering that there are also many small $B_4C$ grains present at the boundaries of TiB$_2$ grains, the holes are attributed to the pullout of the small $B_4C$ grains. This means that there is also intergranular fracture for the $B_4C$ grains. As

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Figure 2. Relative densities of as-prepared TiB$_2$–$B_4C$ composites.
a typical brittle ceramic, monolithic $B_4C$ normally shows a transgranular fracture with a very low toughness. However, when $B_4C$ and TiB$_2$ combine to form a TiB$_2$–$B_4C$ composite, due to their large difference in thermal expansion coefficient and Young’s modulus, there is residual stress between the two phases and results in microcracks around boundaries [27]. At this situation, it is possible that the main crack will connect the microcracks, so that the $B_4C$ grain shows an intergranular fracture.

Figure 6 shows the bending strength of TiB$_2$–$B_4C$ composites prepared from $B_4C$ powders with different particle size. Whether the content of $B_4C$ is 20 vol% or 30 vol%, the bending strength of the composite first increases and then decreases with increasing $B_4C$ powder particle size. For the composites prepared from the $B_4C$ powders with the same particle size, the
The addition of 30 vol% B₄C results in higher strength than 20 vol% B₄C. When the particle size of the used B₄C powders is 0.5 µm, the bending strength of the composite is the lowest, which is ascribed to the lowest relative density, as shown in Figure 2. When using 3.12 µm B₄C, the obtained TiB₂–30 vol% B₄C exhibits the maximum value of 671 MPa. According to the Griffith equation [28], the fracture strength of the ceramic composite is inversely proportional to its critical flaw size which is often taken as the characteristic grain size [29]. Figures 2–4 demonstrate that TiB₂–30 vol% B₄C composite prepared from 3.12 µm B₄C powder is fully densified with the finest and most homogenous microstructure, which contributes its highest strength.

The Vickers hardness of TiB₂–B₄C composites prepared B₄C powders with different particle sizes is presented in Figure 7. The measured Vickers hardness is associated to the phase composition, the relative density and the grain size, as well as the indentation load. Due to the higher intrinsic hardness of B₄C (~30 GPa) than that of TiB₂ (~25 GPa), the hardness of TiB₂–30 vol% B₄C composites is above than that of TiB₂–20 vol% B₄C composites. When the B₄C content is 20 vol%, the composite prepared from 3.12 µm B₄C...
C powders has the highest hardness because of its full densification. Although the relative density of TiB$_2$–20 vol% B$_4$C composite prepared from 0.5 µm B$_4$C powder is lower than that of composite from 7.09 µm B$_4$C powder, the hardness of the former is a little higher than the latter. When compared Figure 2(a) and (e), it is found the microstructure of the former is finer than that of the latter. According to Lee’s report on B$_4$C ceramic [30], smaller grain size induces greater concentration of grain boundaries and make the moving dislocations encounter grain boundaries with higher frequency, which requires larger stresses for further deformation and results in higher measured hardness. Therefore, for TiB$_2$–20 vol % B$_4$C composites, finer microstructure and smaller grain sizes affects the measured density more than the relative density. Despite the different particle size of the used raw B$_4$C powder, the hardness of prepared TiB$_2$–30 vol% B$_4$C composites keep at around 28 GPa.

Figure 8 shows the fracture toughness of TiB$_2$–B$_4$C composites prepared from B$_4$C powders with different particle sizes. The fracture toughness was measured by the indentation fracture method and the presence of pores would prevent crack propagation which enhanced the measured values. When the used B$_4$C powder is 0.5 µm, due to their lower densities, the measured toughness of the composites are higher. Meanwhile, when the used B$_4$C powders are 3.12 µm and 7.09 µm, the obtained composites are all nearly fully densification and the measured toughness are not affected by the pores. In this case, it is found that the particle size of raw B$_4$C powder has small influence on the fracture toughness of the composites. Moreover, TiB$_2$–20 vol% B$_4$C composites perform better on the toughness than TiB$_2$–30 vol% B$_4$C composites. This can be explained by the brittle instincts and the transgranular fracture mode of B$_4$C ceramics [31,32]. The toughness of TiB$_2$–B$_4$C composites was around 4 MPa·m$^{1/2}$, which was higher than that of monolithic B$_4$C ceramic (2–3 MPa·m$^{1/2}$). The thermal expansion coefficients of B$_4$C and TiB$_2$ are different, which induces residual stress during the cooling process. Skorokhod et al. [33] estimated the residual stress between B$_4$C and TiB$_2$ grains, and the value was as high as ~1 GPa, which is strong enough to break the interface and cause microcracking. Typical toughening mechanisms such as crack deflection, crack bridging and crack branching could be observed along the crack propagation path in Figure 9.

4. Conclusions

The effects of B$_4$C content and particle size on the relative density, phase composition, microstructure and mechanical performance of TiB$_2$–B$_4$C composites fabricated via the hot pressing were investigated. The addition of B$_4$C to TiB$_2$ matrix prevented the orientation of TiB$_2$ grains by pinning effect during the sintering process. However, when using more B$_4$C powder with smaller particle size, more B$_2$O$_3$ was introduced,
which improved the orientation and coarsened the composites. As a result, TiB$_2$–B$_4$C composites prepared from 0.50 μm B$_4$C powders only got a maximum relative density of 97.2% at 20 vol% B$_4$C and decreased to 92.3% at 30 vol% B$_4$C. Meanwhile, all composites with 20–30 vol% B$_4$C prepared from 3.12 μm and 7.09 μm B$_4$C powders were nearly fully densified. Due to the higher hardness and lower toughness of B$_4$C, the addition of more B$_4$C to TiB$_2$ matrix enhanced the hardness but declined the toughness. When the B$_4$C particle size was 3.12 μm, the obtained TiB$_2$–30 vol% B$_4$C composites resulted in the optimal mechanical performance. The bending strength, Vickers hardness, fracture toughness were 671 MPa, 27.93 GPa, and 3.91 MPa·m$^{1/2}$, respectively.

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Disclosure statement

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