Effects of HfB$_2$ and HfN Additions on the Microstructures and Mechanical Properties of TiB$_2$-Based Ceramic Tool Materials

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Abstract: The effects of HfB$_2$ and HfN additions on the microstructures and mechanical properties of TiB$_2$-based ceramic tool materials were investigated. The results showed that the HfB$_2$ additive not only can inhibit the TiB$_2$ grain growth but can also change the morphology of some TiB$_2$ grains from bigger polygons to smaller polygons or longer ovals that are advantageous for forming a relatively fine microstructure, and that the HfN additive had a tendency toward agglomeration. The improvement of flexural strength and Vickers hardness of the TiB$_2$-HfB$_2$ ceramics was due to the relatively fine microstructure; the decrease of fracture toughness was ascribed to the formation of a weaker grain boundary strength due to the brittle rim phase and the poor wettability between HfB$_2$ and Ni. The decrease of the flexural strength and Vickers hardness of the TiB$_2$-HfN ceramics was due to the increase of defects such as TiB$_2$ coarse grains and HfN agglomeration; the enhancement of fracture toughness was mainly attributed to the decrease of the pore number and the increase of the rim phase and TiB$_2$ coarse grains. The toughening mechanisms of TiB$_2$-HfB$_2$ ceramics mainly included crack bridging and transgranular fracture, while the toughening mechanisms of TiB$_2$-HfN ceramics mainly included crack deflection, crack bridging, transgranular fracture, and the core-rim structure.

Keywords: TiB$_2$-HfB$_2$ ceramics; TiB$_2$-HfN ceramics; hot-pressed sintering; microstructure; mechanical properties

1. Introduction

In recent years, with the widespread use of difficult-to-machine materials in engineering, cutting tools have faced the challenge of machining these materials under high speed, which requires that the tools have high hardness, excellent wear resistance, oxidation resistance, and so on. However, compared with the ceramic tool materials, the traditional tool materials (high-speed steel and cemented carbide) showed a lower red hardness in machining these difficult-to-machine materials, which did not meet the need of high speed machining. Recently, ceramic tools—Al$_2$O$_3$-based, Si$_3$N$_4$-based, and TiB$_2$-based ceramic tools—exhibited excellent cutting performance in machining the difficult-to-machine materials such as martensitic stainless steel, Inconel 718, ultra-high-strength steel 300 M, heat-treated AISI4140, hardened Cr12MoV mold steel, and Invar36 alloy [1–6]. The TiB$_2$-based ceramic tool exhibited higher hardness compared with the other ceramic tools, which was attributed
to the higher hardness of TiB₂ ceramic than that of the other ceramics. TiB₂ also has a high melting point, excellent wear resistance, and oxidation resistance, which can also be applied in other fields such as manufacturing armor plates and dies [7–10]. However, it shows a tendency toward low flexural strength and low fracture toughness, which limits the more widespread application of TiB₂. In order to reverse this tendency and improve the mechanical properties of TiB₂ ceramic, reinforcements such as hard phases, metal phases, and whiskers have been employed to fabricate TiB₂-based ceramic materials through spark plasma sintering, vacuum hot-pressed sintering, or reactive hot-pressed sintering.

Usually, the hard phases included TaC, TiSi₂, Al₂O₃, WC, Ti₃C, B₄C, NbC, MoSi₂, SiC, and ZrB₂ [9–16], which could inhibit the grain growth of the base material to obtain a fine microstructure. HfB₂ and HfN have high hardness, high melting point, and high oxidation resistance, and as reinforcements they can enhance the mechanical properties of ceramics such as ZrB₂-CrSi₂-HfB₂, ZrB₂-SiC-HfB₂, B₄C-HfB₂, and SiBCN-HfN [17–20], which make them potential candidate reinforcements for ceramic tool materials. In addition, because HfB₂ and HfN have better thermal stability to resist deformation and decomposition at elevated temperature, they may improve the cutting performance and working life of TiB₂-based ceramic tools. The metal phases often contain Fe, Co, Ni, and Mo [7,12,21,22], which could decrease the sintering temperature and improve the boundary strength among grains and relative density, while the ceramic whiskers such as aluminum borate whiskers and SiC whiskers could change the direction of crack growth to consume more crack propagation energy [23–25], which could improve the flexural strength and fracture toughness. Usually, adopting a combination of reinforcements for fabricating TiB₂-based ceramics can obtain better mechanical properties. In addition, compared with spark plasma sintering that is employed in fabricating the ceramic composites [9,16], vacuum hot-pressed sintering is considered to be easily adaptable and economically viable.

In this paper, TiB₂-HfB₂ and TiB₂-HfN ceramic tool materials will be fabricated with powders of TiB₂, HfB₂, HfN, Mo, and Ni by vacuum hot-pressed sintering. The characteristics of these composites are analyzed according to their microstructures and mechanical properties.

2. Experimental Procedures

Commercially available TiB₂ powder (99.9%, 1 μm, Shanghai Xiangtian Nanomaterials Co., Ltd., Shanghai, China), HfB₂ powder (99.9%, 0.8 μm, Shanghai Chaowei Nanomaterials Co., Ltd., Shanghai, China) and HfN powder (99.9%, 0.8 μm, Shanghai Chaowei Nanomaterials Co., Ltd.) were used as the raw materials. Ni powder (99.8%, 1 μm, Shanghai Yunfu Nanotechnology Co., Ltd., Shanghai, China) and Mo powder (99.8%, 1 μm, Shanghai Yunfu Nanotechnology Co., Ltd.) were added as sintering aids. The compositions of the composite tool materials are shown in Table 1.

| Sample | TiB₂/wt % | HfB₂/wt % | HfN/wt % | Ni/wt % | Mo/wt % |
|--------|-----------|-----------|-----------|---------|---------|
| S1     | 82        | 10        | -         | 4       | 4       |
| S2     | 72        | 20        | -         | 4       | 4       |
| S3     | 62        | 30        | -         | 4       | 4       |
| S4     | 82        | -         | 10        | 4       | 4       |
| S5     | 72        | -         | 20        | 4       | 4       |
| S6     | 62        | -         | 30        | 4       | 4       |
The powders were mixed and milled for 48 h in a polyethylene jar with WC (tungsten carbide) balls and alcohol as the medium. Then the mixed slurry was dried in vacuum and sieved by a 200-mesh sieve. The compacted powders were hot pressed for 30 min at 1650 °C under 30 MPa in a vacuum ((1.2–2.4) × 10⁻³ Pa). The hot pressed samples were cut into testing specimens by the electrical discharge wire cutting method and the surfaces of the testing bars were polished using diamond slurries. The dimensions of the specimens were 3 mm × 4 mm × 40 mm. Flexural strength was measured at a span of 30 mm and a crosshead speed of 0.5 mm/min by the three-point bending test method on an electron universal tester (CREE-8003G, Dongguan City Kerry Instrument Technology Co., Ltd., Dongguan, China), according to Chinese National Standards GB/T 6569-2006/ISO 14704:2000 [26]. The fracture toughness (\(K_{IC}\)) was measured via the direct indentation method and was calculated through the following equation [12,27]:

\[
K_{IC} = 0.203H_Va^{1/2}\left(\frac{c}{a}\right)^{-3/2}
\]

where \(H_V\) is the Vickers hardness, \(2a\) is the length of the impression diagonal, and \(2c\) is the overall indentation crack length including \(2a\). The indenter (HVS-30, Shanghai Precision Instruments Co., Ltd., Shanghai, China) was of Vickers DPH (diamond pyramid hardness) type and the applied static load was 196 N for 15 s. Vickers hardness was measured on the polished surfaces using a diamond pyramid indenter under a load of 196 N by an HV-120 based on Chinese National Standards GB/T 16534-2009 [28]. The relative density of each specimen was measured by the Archimedes method with distilled water as the medium. The theoretical density was calculated according to the rule of mixtures based on the following densities: 4.52, 10.50, 13.80, 8.90, and 10.20 g/cm³ for TiB₂, HfB₂, HfN, Ni, and Mo, respectively. At least 15 specimens were tested for each experimental condition. X-ray diffraction (XRD, EMPYREAN, PANalytical B.V., Almelo, Netherlands) and energy dispersive spectrometry (EDS, ACT-350, Oxford Instruments, Oxford, UK) were used to analyze the compositions of the composite. Scanning electron microscopy and back scattered electron microscopy (SEM, BSE, Supra-55, Carl Zeiss AG, Oberkochen, Germany) were used to observe the polished surface and fractured surface morphologies.

3. Results and Discussions

3.1. Microstructure

Figure 1 shows the XRD patterns of the TiB₂-HfB₂ and TiB₂-HfN ceramic tool materials. The major crystal phases are TiB₂ and HfB₂ in the TiB₂-HfB₂ ceramics, and TiB₂ and HfN in the TiB₂-HfN ceramics. The minor phase is the Ni₃Mo intermetallic compound in the TiB₂-HfB₂ and TiB₂-HfN ceramic tool materials. This is because Ni and Mo can form the Ni₃Mo intermetallic compound at 1300 °C [29]. The Ni₃Mo intermetallic compound has a high melting point of about 1320 °C, so it may be a promising high-temperature structural material [30]. Compared with the standard peaks, the peaks of HfB₂ are offset about two degrees to the right and are near the peaks of TiB₂. This indicates there is likely an exchange of Ti and Hf atoms in the sintering, which leads to a complex solid solution of TiB₂ and HfB₂ formed in the ceramic tool materials. The peaks of HfN are in accordance with the standard peaks.
polishing process, which indicates that a weaker grain boundary strength formed in these ceramics. Not only can the HfB\(_2\) additive inhibit the growth of TiB\(_2\) grains but can also change the morphology of some TiB\(_2\) grains, and in Figure 2d–f the HfN grain agglomeration becomes more serious leading to the formation of more TiB\(_2\) coarse grains and pores. This indicates that the HfB\(_2\) additive not only can inhibit the growth of TiB\(_2\) grains but can also change the morphology of some TiB\(_2\) grains, and that the HfN additive exhibits a tendency toward agglomeration.

Figure 2d–f. In terms of size and shape, the pores in Figure 2a–c are bigger than that in Figure 2d–f; the regular pore shape in Figure 2a–c looks like the TiB\(_2\) grain shape and the irregular pore shape in Figure 2d–f looks like the shape of agglomerated HfN grains possibly pulled out in the grinding and polishing process, which indicates that a weaker grain boundary strength formed in these ceramics in the sintering processing. Moreover, in Figure 2a–c the morphology of some TiB\(_2\) grains changes from bigger polygons to smaller polygons or longer ovals which is advantageous for the formation of a relatively fine microstructure, and in Figure 2d–f the HfN grain agglomeration becomes more serious leading to the formation of more TiB\(_2\) coarse grains and pores. This indicates that the HfB\(_2\) additive not only can inhibit the growth of TiB\(_2\) grains but can also change the morphology of some TiB\(_2\) grains, and that the HfN additive exhibits a tendency toward agglomeration.

Figure 1. XRD patterns of TiB\(_2\)-HfB\(_2\) and TiB\(_2\)-HfN ceramic tool materials.
Figure 2. SEM-BSE photographs of the polished surfaces of TiB$_2$-HfB$_2$ and TiB$_2$-HfN ceramic tool materials: (a) TiB$_2$-10 wt \% HfB$_2$; (b) TiB$_2$-20 wt \% HfB$_2$; (c) TiB$_2$-30 wt \% HfB$_2$; (d) TiB$_2$-10 wt \% HfN; (e) TiB$_2$-20 wt \% HfN; (f) TiB$_2$-30 wt \% HfN.

Figure 3. EDS of the phases in the TiB$_2$-HfB$_2$ ceramic tool materials: (a) EDS of the dark phase; (b) EDS of the white phase, and EDS of the phases in the TiB$_2$-HfN ceramic tool materials; (c) EDS of the dark phase; (d) EDS of the white phase; (e) EDS of the grey phase.

Figure 4 shows the fracture morphology of the TiB$_2$-HfB$_2$ and TiB$_2$-HfN ceramic tool materials. As can be seen in Figure 4a–c, with increasing HfB$_2$ content from 10 wt \% to 30 wt \%, the TiB$_2$ grains become smaller; meanwhile, the TiB$_2$ grain shapes exhibit the same variation trend as presented in Figure 3a–c; moreover, the pore number decreases progressively. However, in Figure 4d–f with increasing HfN content from 10 wt \% to 30 wt \%, the TiB$_2$ grains become larger leading to the formation of coarse TiB$_2$ grains; and the pore number decreases progressively. The results indicate that the HfB$_2$ additive can not only inhibit the growth of the TiB$_2$ grains, but can also change the microstructure of TiB$_2$-based ceramic, and that the HfN additive cannot inhibit the TiB$_2$ grain growth.
As can be seen, their relative densities increase with increasing HfB₂ and HfN contents from 10 wt % to 30 wt %, respectively. The relative density increments of the TiB₂-HfB₂ ceramics are smaller, and the relative density variation curve is relatively flat, while the relative density variation curve of TiB₂-HfN shows a bigger increment in relative density at first, and then finally shows a smaller increment. These results are ascribed to the pore number reduction with increasing the additive content, to some extent, and is derived from the higher sintering pressure (30 MPa) and the metal phases (Ni and Mo) that can efficiently reduce the sintering temperature and can accelerate the densification of these ceramics. As a consequence, their relative densities with the addition of HfB₂ or HfN can be improved, and when the HfB₂ and HfN contents are 30 wt %, the optimal relative densities of the TiB₂-HfB₂ and TiB₂-HfN ceramics are 99.0% ± 0.2% and 99.4% ± 0.3%, respectively.

Figure 5 presents the relative densities of the TiB₂-HfB₂ and TiB₂-HfN ceramic tool materials. As can be seen, their relative densities increase with increasing HfB₂ and HfN contents from 10 wt % to 30 wt %, respectively. The relative density increments of the TiB₂-HfN ceramics are smaller, and the relative density variation curve is relatively flat, while the relative density variation curve of TiB₂-HfB₂ shows a bigger increment in relative density at first, and then finally shows a smaller increment. These results are ascribed to the pore number reduction with increasing the additive content, to some extent, and is derived from the higher sintering pressure (30 MPa) and the metal phases (Ni and Mo) that can efficiently reduce the sintering temperature and can accelerate the densification of these ceramics. As a consequence, their relative densities with the addition of HfB₂ or HfN can be improved, and when the HfB₂ and HfN contents are 30 wt %, the optimal relative densities of the TiB₂-HfB₂ and TiB₂-HfN ceramics are 99.0% ± 0.2% and 99.4% ± 0.3%, respectively.

**Figure 4.** Fracture morphology of TiB₂-HfB₂ and TiB₂-HfN ceramic tool materials: (a) TiB₂-10 wt % HfB₂; (b) TiB₂-20 wt % HfB₂; (c) TiB₂-30 wt % HfB₂; (d) TiB₂-10 wt % HfN; (e) TiB₂-20 wt % HfN; (f) TiB₂-30 wt % HfN.

**Figure 5.** Relative densities of TiB₂-HfB₂ and TiB₂-HfN ceramic tool materials.
3.2. Mechanical Properties

Figure 6 exhibits the variation of the mechanical properties of the TiB$_2$-HfB$_2$ ceramics with changes of the HfB$_2$ content and variation of the mechanical properties of the TiB$_2$-HfN ceramics with changes of the HfN content. In Figure 6a, with the increase of the HfB$_2$ content from 10 wt % to 30 wt %, the flexural strength increases from 680.49 ± 15 MPa to 708.71 ± 18 MPa; Vickers hardness increases from 19.15 ± 0.21 GPa to 21.52 ± 0.24 GPa; however, the fracture toughness decreases from 6.92 ± 0.18 MPa·m$^{1/2}$ to 5.53 ± 0.18 MPa·m$^{1/2}$. The TiB$_2$-30 wt %HfB$_2$ ceramic tool material exhibits better mechanical properties including flexural strength of 708.71 ± 18 MPa, which is higher than 533 MPa (the flexural strength of TiB$_2$-TaC ceramics [9]), Vickers hardness of 21.52 ± 0.24 GPa that is higher than 19.8 ± 0.6 GPa (Vickers hardness of the TiB$_2$-SiC-CNTs ceramics [8]), and fracture toughness of 5.53 ± 0.18 MPa·m$^{1/2}$ that is higher than 5.2 MPa·m$^{1/2}$ (fracture toughness of the TiB$_2$-SiC ceramics [31]). The improvement of flexural strength and Vickers hardness is due to the relatively fine microstructure, which is in agreement with the result that the fine microstructure can improve the mechanical properties of ceramic composite materials [32]. As the HfB$_2$ content increases, the fracture toughness decreases gradually, which can be ascribed to the increase of the brittle rim phase. The reason is that the rim phase is mainly the complex solid solution of TiB$_2$ and HfB$_2$, which may be a brittle phase; moreover, the wettability between HfB$_2$ and Ni (the wettability angle: ~99°) is poor.

In Figure 6b, with the increase of the HfN content from 10 wt % to 30 wt %, the flexural strength decreases from 813.69 ± 21 MPa to 716.37 ± 23 MPa; the Vickers hardness decreases from 22.59 ± 0.24 GPa to 19.23 ± 0.23 GPa; however, the fracture toughness increases from...
6.32 ± 0.16 MPa·m$^{1/2}$ to 7.52 ± 0.17 MPa·m$^{1/2}$. The TiB$_2$-10 wt % HfN ceramic tool material shows better mechanical properties, including flexural strength of 813.69 ± 21 MPa that is higher than 705 MPa (flexural strength of the TiB$_2$-10 wt % SiC ceramics [6]), Vickers hardness of 22.59 ± 0.24 GPa which is higher than 21.85 GPa (Vickers hardness of the TiB$_2$-TiC-10 wt % Ni ceramics [33]), and fracture toughness of 6.32 ± 0.16 MPa·m$^{1/2}$ that is higher than 6 MPa·m$^{1/2}$ (fracture toughness of the TiB$_2$-2.5 wt % MoSi ceramics [15]). The decrease of the flexural strength and Vickers hardness is due to the increase of the defects such as the TiB$_2$ coarse grain and HfN agglomeration; this indicates that the defects have more negative effects on the flexural strength and Vickers hardness than the core-rim structure, although the core-rim structure is advantageous for improving the mechanical properties. The enhancement of fracture toughness is mainly attributed to the decrease of the pore number and the increase of the rim phase and TiB$_2$ coarse grain; decreasing the pore formation can keep the cracks from growing, which will improve fracture toughness; the rim phase of TiB$_2$-HfN ceramics exhibits a higher grain boundary strength than the rim phase of TiB$_2$-HfB$_2$ ceramics, which will provide a larger grain growth resistance for enhancing fracture toughness; in addition, TiB$_2$ coarse grains can consume more fracture energy in the fracturing process even though the TiB$_2$ is a brittle phase, which leads to the improvement of the fracture toughness.

In order to further analyze the toughening mechanisms of TiB$_2$-HfB$_2$ and TiB$_2$-HfN ceramics, the crack propagation paths are shown in Figure 7. As can be seen, the crack propagation path in Figure 7a is straighter than that in Figure 7b; the crack deflection in Figure 7b is more obvious than that in Figure 7a; crack bridging and transgranular fracture play an important role in Figure 7a, while crack deflection, crack bridging, and transgranular fracture occupy important positions in Figure 7b, which are advantageous for enhancing fracture toughness and are the main toughening mechanisms of these ceramics. Much fracture energy will be consumed by crack bridging because crack bridging as well as crack deflection can change the direction of crack propagation (see the red circles in Figure 7), which is advantageous for improving fracture toughness. Usually the formation of the rim phase is propitious to the enhancement of fracture toughness, but in Figure 7a the rim phase shows a brittle characteristic leading to lower fracture toughness with increasing HfB$_2$ content as mentioned above; moreover, the relatively straight crack crossing the rim phase and TiB$_2$ grain will consume less fracture energy, which is harmful to the improvement of fracture toughness. However, intergranular fracture and transgranular fracture coexisted in Figure 7b, where the crack path is full of twists and turns which is advantageous to enhancing fracture toughness.

![Figure 7. Crack propagation path of the TiB$_2$-HfB$_2$ (a) and TiB$_2$-HfN (b) ceramic tool materials.](image_url)
4. Conclusions

TiB$_2$-based ceramic tool materials reinforced by HfB$_2$ and HfN additives have been fabricated by hot pressed sintering. The effects of HfB$_2$ and HfN additions on their microstructures and mechanical properties were investigated. The results showed that the HfB$_2$ additive can inhibit the TiB$_2$ grain growth and can change the morphology of some of the TiB$_2$ grains from bigger polygons to smaller polygons or longer ovals, which is favorable for the formation of a relatively fine microstructure, while the HfN additive tends to agglomerate. With increasing HfB$_2$ and HfN contents from 10 wt % to 30 wt %, the relative densities of these ceramics increased gradually. The relatively fine microstructure improved the flexural strength and Vickers hardness of the TiB$_2$-HfB$_2$ ceramics. The poor wettability between HfB$_2$ and Ni resulted in the formation of weak grain boundary strength and the complex solid solution of TiB$_2$-HfB$_2$ is a brittle phase, which led to the decrease of fracture toughness of the TiB$_2$-HfB$_2$ ceramics. The increase of the defects such as the TiB$_2$ coarse grain and HfN agglomeration resulted in the decrease of the flexural strength and Vickers hardness of the TiB$_2$-HfN ceramics; the decrease of the pore number and the increase of the rim phase and TiB$_2$ coarse grain are advantageous for the enhancement of fracture toughness. The toughening mechanisms of the TiB$_2$-HfB$_2$ ceramics mainly included crack bridging and transgranular fracture, while the toughening mechanisms of the TiB$_2$-HfN ceramics mainly included crack deflection, crack bridging, transgranular fracture, and the core-rim structure. The TiB$_2$-30 wt % HfB$_2$ ceramic tool material exhibited better mechanical properties including a flexural strength of 708.71 ± 18 MPa, Vickers hardness of 21.52 ± 0.24 GPa, and fracture toughness of 5.53 ± 0.18 MPa·m$^{1/2}$. The TiB$_2$-10 wt % HfN ceramic tool material showed better mechanical properties including a flexural strength of 813.69 ± 21 MPa, Vickers hardness of 22.59 ± 0.24 GPa, and fracture toughness of 6.32 ± 0.16 MPa·m$^{1/2}$.

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Conflicts of Interest: The authors declare no conflict of interest.

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