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Ultrahigh temperature ceramics (UHTCs) based on ZrB₂ and HfB₂ systems: powder synthesis, densification and mechanical properties

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Abstract. Phase pure ZrB_2 and HfB_2 powders were synthesized by boro/carbothermal reduction (BCTR) of ZrO_2 and borothermal reduction of HfO_2 , respectively. Combining the thermodynamic calculations and XRD results, the reaction process of BCTR of synthesized ZrB_2 powder was shown. The ZrB_2 powder synthesized at 1650 °C showed a better sinterability, due to its smaller particle size and lower oxygen content. Most of the HfB_2 particles obtained at 1600 °C presented nearly column-like morphology with 1-1.5µm size. Using the synthesized HfB₂ powder and commercial α -SiC, hot-pressed HfB₂-20 vol.% SiC composite has high flexural strength of 993 ±90 MPa and fracture toughness of 6.29±0.65 MPa·m^{1/2}, which were significantly higher than the reported values in literature.

1. Introduction

Ultrahigh temperature materials (UHTMs) are a family of materials that are chemically and physically stable at high temperatures and in reactive atmospheres. The characteristics of UHTMs allow them to be used in extreme environments including those associated with hypersonic flight, atmospheric re-entry, and rocket propulsion [1]. The UHTMs includes carbon/carbon composites, refractory metals, and refractory ceramic compounds (such as carbides, borides and nitrides). The carbon/carbon composites and tungsten alloy were successfully installed on X-43A vehicle that flew at Mach 7 in March 2004 as part of the Hyper-X program [2]. However, due to the poor oxidation resistance of the carbon/carbon composites and high density of the tungsten alloy, interest in refractory ceramic compounds characterized by high melting points, high electrical and thermal conductivities, high hardness, and good chemical inertness and oxidation resistance, has increased significantly in recent years, especially transition metal diborides with the relatively good oxidation resistance [3-4]. Of the

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transition metal diborides, zirconium diboride (ZrB₂) and hafnium diboride (HfB₂) are identified as the most promising candidates for high temperature applications such as nose caps, sharp leading edges, vanes and similar objects for use in high velocity flight or on future generations of reentry vehicles [3-5]. It has been shown that addition of SiC to diborides ceramics results in significant improvements in oxidation resistance and mechanical properties compared to diborides alone [6-10]. Hot-pressed HfB₂-20 vol.%SiC ceramics was flown on NASA-funded hypervelocity slender-body flight tests, as small radius nose tips, in 1997 during the SHARP-B1 program and as components of leading-edge strakes in 2000 during the SHARP-B2 program, which successfully showed the non-ablating performance of borides ceramics [11].

Because of the strong covalent bonding and low self-diffusion, high temperatures and external pressures are required to densify diborides [12]. Two ways typically are used to enhance densification. The first way is that alternative processing routes, such as reactive hot pressing [13-15], spark plasma sintering [16-17], and polymer precursors [18-19] have been investigated to improve the purity and densification behavior of diborides. The second way is that various additives have been studied to reduce sintering temperature. For example, the addition of metals (Ni) or ceramics (Si₃N₄, ZrN, Yb₂O₃ and VC) as sintering aids has been proven to enhance the sinterability and densification of ZrB₂-SiC ceramics [20-25]. Grain boundary phases deriving from the sintering aids often drastically deteriorate the elevated temperature strength and other mechanical properties [26-27]. Therefore, study on the preparation of MB₂-based ceramics from fine starting powders with high sinterability and high purity without adding sintering additives is very significant. However, most of the current commercially available powders have coarse particle size and demonstrate poor sinterability. In order to improve sinterability, pulverization is generally used to decrease the particle size. However, impurities are introduced, especially oxygen from the surface oxidation of particles, which significantly deteriorates the densification behavior and ceramic properties [28-29].

In this work, we carried out the synthesis of ZrB_2 powder via boro/carbothermal reduction (BCTR) of ZrO_2 with B_4C and carbon in vacuum, where the characterization of powder morphology and sinterability was investigated. On the other hand, highly active HfB₂ powder was synthesized by borothermal reduction of HfO₂ using amorphous boron. To reflect the performance of synthesized HfB₂ powder compared with commercially available powders, HfB₂-20 vol.%SiC composite was prepared by hot pressing at 2000 °C followed by characterization of microstructures and mechanical properties.

2. Experimental Procedure

The raw materials used in this study were ZrO_2 ($D_{50}=0.6 \,\mu\text{m}$, CSG Holding Co., Ltd, Shenzhen, China), HfO₂ ($D_{50}=0.25\,\mu\text{m}$, Found Star Science and Technology Co., Ltd, Beijing, China), B₄C ($D_{50}=1.5\,\mu\text{m}$, Jingangzuan Boron Carbide Co., Ltd, Mudanjiang, China), carbon ($D_{50}=1.5\,\mu\text{m}$), α -SiC ($D_{50}=0.45\,\mu\text{m}$, Changle Xinyuan Carborundum Micropowder Co. Ltd, Changle, China), and amorphous boron (average particle size <1 μ m, Dandong Chemical Engineering Institute Co. Ltd., Dandong, China), with purities of 99.8 %, 96 %, 99 %, 99 %, 98.5 % and 96 %, respectively. The ZrO₂, B₄C and carbon were used as starting powders to synthesize ZrB₂ based on the boro/carbothermal reduction. The HfO₂ and boron were used as starting powders to synthesize HfB₂

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powder based on the borothermal reduction. First the starting mixtures were mixed for 24 h in a polythene bottle using ethanol and Si_3N_4 balls, and dried by rotary evaporation. After being dried, the powder mixtures were dry pressed into disks. Then the disks were heated at a rate of 10 °C/min to the desired temperature and held for 60 min in vacuum. The powder synthesis was conducted using a graphite crucible in a resistance-heated graphite element furnace.

To evaluate the ZrB_2 sinterability, the densification process of the synthesized powder was performed by pressureless sintering in the temperature range of 1900-2100 °C for 2 h. Firstly, as-prepared ZrB_2 powder was uniaxially pressed at a pressure of 30 MPa for 60 s. Cold isostatic pressing with an applied pressure of 300 MPa for 120 s was subsequently conducted. Powder compacts were heated to 1650 °C with a heating rate of 15 °C/min in the graphite element furnace under vacuum. Then 60 min isothermal hold at 1650 °C was used for the recovery of the vacuum (~5 Pa). After 60 min at 1650 °C, the furnace was backfilled with argon and heated at 30 °C/min to the desired sintering temperature.

Using the as-synthesized HfB₂ and commercially available α -SiC, HfB₂-20 vol.% SiC composite was hot pressed at 2000 °C under a pressure of 30 MPa. The specimen was heated from room temperature to 1650 °C with a heating rate of 8 °C/min under vacuum. Above 1650 °C, the furnace was backfilled with argon and heated at 15 °C/min to 2000 °C, followed by a 1h dwell, and then cooled to room temperature naturally. The application of pressure was only at the highest temperature.

Phase composition was determined by X-ray diffraction (XRD, D/max 2550 V, Tokyo, Japan). The relative amounts of the phases were quantified using *K* value method [30]. Morphology of the synthesized powder was characterized by scanning electron microscope (SEM, Hitachi S-570, Tokyo, Japan). Oxygen content was determined by a Nitrogen/Oxygen Determinator (TC600, Leco Corporation, St. Joseph, MI). Particle size distribution was analyzed using a laser particle size analysis (*Zeta Plus*). The hardness and fracture toughness were measured by the indentation method (Wilson-Wolpert Tukon2100B, USA), using a load of 5 kg for 10 s on a polished surface. Flexural strength was measured by a 3-point bending test (test bars 2.5 mm×2 mm×25 mm) with a span of 20mm.

3. Results and discussion

3.1. Boro/carbothermal reduction synthesis of ZrB_2 and pressureless densification The ZrB_2 powder was synthesized according to boro/carbothermal reduction reaction:

$$2ZrO_2 + B_4C + 3C \rightarrow 2ZrB_2 + 4CO \tag{1}$$

Figure 1 showed the XRD patterns of the synthesized ZrB_2 powder at different temperatures via BCTR of ZrO_2 with B_4C and carbon based on stoichiometric proportion of the reaction (1). Both ZrB_2 and ZrC phase were present in the synthesized powder. To understand the reason why ZrC phase also remained in the synthesized powder, the reaction process was firstly explored.



Figure 1. XRD patterns of the synthesized ZrB_2 powder at different temperatures according to stoichiometric proportion of the reaction (1).

Compared to reaction (1), previous studies have shown that ZrO_2 could react with B_4C at lower temperatures [12]:

$$7ZrO_2 + 5B_4C \rightarrow 7ZrB_2 + 3B_2O_3 + 5CO \tag{2}$$

Then the product B_2O_3 of reaction (3) continues to react with ZrO_2 and carbon to form $ZrB_2[31]$:

$$ZrO_2 + B_2O_3 + 5C \rightarrow ZrB_2 + 5CO \tag{3}$$

Favorability of reaction is determined based on the sign of change of the Gibbs free energy. When it is negative, the reaction becomes favourable. In standard state (pCO= 1.013×10^5 Pa), reactions (1)-(3) become favorable above 1424 °C, 1218 °C and 1509 °C, respectively (figure 2(a)). In the present study, the synthesis of ZrB₂ powder was conducted in vacuum. The CO product was constantly removed by the pumping, and the furnace pressure remained below 11 Pa during the whole reduction process. Assuming a CO partial pressure of 11 Pa, reactions (1)-(3) are thermodynamically favorable above 894 °C, 784 °C and 938 °C, respectively (figure 2(b)). High vacuum markedly decreased the starting temperature of the above reactions. Observing the reaction (3), the intermediate B₂O₃ product played an important role in the synthesis of ZrB₂. In fact, B₂O₃ has an unusually low melting point (450 °C) and a high vapor pressure. The vapor pressure of B₂O₃ at 1527 °C reached 344 Pa, leading to its rapid vaporization [32]. According to reaction (2), the deficiency of B₂O₃ meant the excess of ZrO₂ and carbon, which would form ZrC phase based on the reaction:

$$ZrO_2 + 3C \to ZrC + 2CO \tag{4}$$

Therefore, the presence of ZrC phase in the synthesized powder was mainly attributed to the vaporization of intermediate B_2O_3 product. Though minimum favorable temperature of reaction (4) was 1065 °C under 11 Pa pressure, its Gibbs' free energy value did not show significantly more negative, compared to reactions (1)-(3) (figure 2(b)). So the ZrC phase appeared at relative high temperatures.

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Figure 2. The change in Gibbs' free energy of reaction as a function of temperature for reactions (1)-(5) under the standard state (a) and 11 Pa pressure (b).



Figure 3. XRD patterns of the synthesized ZrB_2 powder at 1650°C with different amounts of B_4C in excess.

In order to eliminate ZrC phase, the B_2O_3 loss could be compensated by a substantial excess of B_4C . At the same time, due to the presence of element C in B_4C , the amount of raw carbon should be decreased. Figure 3 showed the XRD patterns of the synthesized powder by adjusting the starting amounts of B_4C and carbon. With the increase of B_4C , ZrC phase gradually decreased. When B_4C was in a 20-25 wt% excess, the ZrC phase disappeared and only ZrB₂ phase existed in powder.

XRD patterns of the synthesized powder with starting B_4C in excess of 20-25 wt% at different temperatures for 1 h were shown in figure 4. With the increase of temperature, a peculiar phenomenon occurred in XRD patterns. The ZrC phase was detected at 1550 °C, but disappeared at 1650 °C. The formation of ZrC should be based on the reaction (4). Due to the presence of enough boron, the ZrC phase could be consumed by the reaction with B_2O_3 and carbon:

$$ZrC + B_2O_3 + 2C \to ZrB_2 + 3CO \tag{5}$$

Thermodynamic calculation showed the minimum favorable temperature of reaction (5) is 806 $^{\circ}$ C under 11 Pa pressure (figure 2(b)). Finally, ZrC phase disappeared at 1650 $^{\circ}$ C, leaving pure ZrB₂ powder.



Figure 4. XRD patterns of the synthesized ZrB_2 powder at different temperatures with B_4C in 20-25 wt% excess.

From figure 4, pure ZrB_2 powder was obtained above 1650 °C. The ZrB_2 powder synthesized at 1650 °C and 1750 °C was referred to as Z6 and Z7, respectively. Figure 5 showed the SEM images of Z6 and Z7 powder. SEM observation did not demonstrate remarkable difference between the Z6 and Z7 powder. However, it can be found that there was a tendency for the particle size and particle morphology with temperature increase, that is, most of the ZrB_2 particles obtained at 1650 °C presented nearly spherical-like with smaller size. When temperature reached 1750 °C, the ZrB_2 powder showed nearly column-like with increasing size. The oxygen content of Z6 and Z7 powder had no obvious difference and was about 0.7 wt%.

Table 1 lists the relative densities of the ZrB₂ ceramics by pressureless sintering in the temperature range of 1900-2100 °C for 2 h using Z6 and Z7 powder. For convenient comparison, the reported results for the pressureless sintered ZrB₂ ceramics from pure commercial ZrB₂ powder were also listed in table 1 [29,33]. The decrease in particle size would result in a higher driving force for densification during pressureless sintering [29,33-34]. Therefore, the Z6 powder showed better sinterability when compared to the Z7 powder as well as the commercial ZrB₂ powder used by Fahrenholtz et al.. The surface oxygen contamination of ZrB₂ particles, in the form of B₂O₃ and ZrO₂, evidently inhibited the densification [35]. Reducing the oxygen content of ZrB₂ powder could enhance densification. Zhang et al. have shown that the relative densities of ZrB₂ increased from 53.8 % to 63.6 % at 1850 °C by pressureless sintering, with the reduction of oxygen content from 3 % to 2 % [34]. So, compared to fine commercial ZrB₂ powder used by Zhu et al., the Z6 powder showed better sinterability due to its lower oxygen content. Accordingly, due to its smaller particle size and lower oxygen content, the synthesized ZrB₂ powder at 1650 °C in this work showed better sinterability.



Figure 5. SEM morphologies of the ZrB₂ powder synthesized at 1650 °C (a) and 1750 °C (b) for 1 h.

Table 1. Relative densities of the ZrB₂ ceramics pressureless sintered at different temperatures for 2 h.

Sample	Particle size Oxygen content		Relative density (%)		
	(µm)	(wt%)	1900 °C	2000 °C	2100 °C
Z6	0.5~1	~0.7	~70	~85	~93
Z7	1~1.5	~0.7	~66	~80	~91
Fahrenholtz et al.[33]	~2.0	~0.9			~78
Zhu et al. [29]	~0.5	~3.0			~70

3.2. Borothermal reduction synthesis of HfB₂ and hot-pressed densification

 HfB_2 is very expensive. consequently, the research on HfB_2 -based ceramics is relatively less at present compared to ZrB_2 . Therefore, it would be very attractive for large-scale synthesis of HfB_2 powders in a convenient and low-cost way. From above boro/carbothermal reduction synthesis of ZrB_2 powder, it is found that some impurities, such as ZrC, may exist in the final products. Therefore, to more easily prepare the pure HfB_2 powder, another potentially more useful method is conducted according to the borothermal reduction reaction using HfO_2 and boron.

Figure 6 showed XRD pattern of the synthesized HfB_2 powder at 1600 °C for 1 h according to stoichiometric proportion by forming B_2O_3 product. In addition to HfB_2 phase, however, the monoclinic HfO_2 was detected, which did not match the theoretical analysis. One rational explanation was that boron sublimated in the form of not only B_2O_3 , but also boron suboxide such as B_2O_2 [36-37], which resulted in the lack of boron and the excess of HfO_2 phase. This analogous phenomenon in the synthesis of HfB_2 powder by carbothermal reduction of HfO_2 with B_4C and graphite was also found in our previous study [30]. Based on the data of XRD, HfO_2 mass fraction was estimated as about 9.7% using the K value method, which meant that there's about 10% boron loss. Figure 7 showed the XRD pattern of the synthesized powder at 1600 °C for 1h with starting boron in excess of 10 wt%, where the HfB_2 powder was referred to as HB10. The XRD pattern showed only hexagonal HfB_2 phase and no evidence of impurities was observed. This indicated that the excess of 10 wt% boron could

compensate boron loss which caused by the sublimation of boron in the form of boron-rich oxides.



Figure 6. XRD pattern of the synthesized HfB_2 powder at 1600 °C for 1 h according to stoichiometric proportion by forming B_2O_3 product.



Figure 7. XRD pattern of the synthesized HfB₂ powder at 1600 °C for 1h with starting boron in excess of 10 wt%.

The oxygen content of the HB10 was 0.79 wt%. The SEM micrograph of the HB10 was shown in figure 8. The as-synthesized HfB₂ powder had a particle size of about 1-1.5 μ m with an equiaxed shape, and had a very narrow diameter distribution, but soft agglomeration appears. Figure 9 was the results of laser particle size analysis. The laser particle size analysis confirmed that the mean diameter and polydispersity of the as-prepared HfB₂ powder HB10 are 1.37 μ m and 0.005, respectively, which was in accordance with the above SEM observation.



Figure 8. SEM morphology of the as-synthesized HfB₂ powder HB10



Figure 9. The size distribution of the as-synthesized HfB₂ powder HB10

The small particle size and uniform diameter distribution is believed to be helpful for further ceramic sintering process to obtain materials with uniform microstructure and high performance. To determine the lowest temperature for reaction completion, heat treatment of HB10 was carried out at 1400 °C and 1500 °C with different holding time successively. However, we found the existence of HfO₂ impurity in the as-prepared HfB₂ powder heat treated both at 1400 °C and 1500 °C, which seems disagree with the thermodynamic calculation. In fact, the thermodynamic calculation can just give out a possibility for a reaction at a certain temperature, but we cannot know whether the reaction could complete or not at that temperature from the thermodynamic calculation. Therefore, heat treatment carried out at 1600 °C or over is necessary to ensure reaction complete. However, it is known that grain grows up and sintering activity decreases as heat-treatment temperature rises. So the HfB₂ powder synthesized at 1600 °C was chosen in the present study.



Figure 10. SEM micrographs of polished surfaces of HBS after acid corrosion

Sample	Raw meterials (vol.%)	Vickers' hardness (GPa)	Flexural strength (MPa)	Fracture toughness (MPam ^{1/2})
HBS	80HfB ₂ +20SiC	20.2±1.0	993±90	6.29±0.65
65# [38]	80HfB ₂ +20SiC	17±0.7	453±46	4.1±0.2
HS [39]	80HfB ₂ +20SiC	17.3	476±46	4.2±0.6
A-HP [40]	77HfB ₂ +20SiC+3HfN	22.3±0.9	650±55	3.8±0.3

Table 2. The starting composition and mechanical properties of the HBS ceramics

The HfB₂-20 vol.% SiC composite was referred to as HBS. Figure 10 showed the SEM micrograph of the polished surface of materials HBS after acid corrosion. The SiC particulates were mainly equiaxed and homogeneously distributed within the diboride skeleton. The average grain size of HfB₂ was estimated as about 2 μ m, which was smaller than that of previous studies [38-39]. The mechanical properties of HBS, including Vickers' hardness, bend strength and fracture toughness, were summarized in table 2. The hardness of HBS was 20.2±1.0 GPa, which was higher than the reported value for HfB₂-20 vol.% SiC [38-39], but slightly lower than the value for HfB₂-20 vol.% SiC-3 vol.% HfN reported by Bellosi et al. (22.3 GPa) [40]. The bending strength of HBS ceramics was 993 ± 90 MPa, which was significantly higher than those reported in literature for HfB₂-20 vol.% SiC materials (450-480 MPa) [38-39]. The fracture toughness for HBS was 6.29±0.65 MPa·m^{1/2}, which was substantially higher than those reported in literature for HfB₂-20 vol.% SiC-3 vol.% MPa·m^{1/2}) [38-40].

4. Summary

Phase pure ZrB_2 and HfB_2 powders were synthesized by boro/carbothermal reduction (BCTR) of ZrO_2 and borothermal reduction of HfO_2 , respectively. Combining the thermodynamic calculations and XRD results, the reaction process of BCTR of synthesized ZrB_2 powder was shown. Compared to the synthesized powder at 1750 °C as well as the commercially available powder used in literature

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reported work, the ZrB₂ powder synthesized at 1650 °C showed a better sinterability due to its smaller particle size and lower oxygen content. Most of the HfB₂ particles obtained at 1600 °C presented nearly column-like morphology with 1-1.5 μ m size. Using the as-synthesized HfB₂ powder and a commercial α -SiC, full HfB₂-20 vol.% SiC composite was prepared by hot pressing. The composite has high flexural strength of 993 ±90 MPa and fracture toughness of 6.29±0.65 MPa·m^{1/2}, which is significantly higher than the reported values in literature.

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