1. Introduction

The high-entropy borides, as a kind of high-entropy ceramic families, have received wide attention for their potential application in many fields such as cutting tool, metallurgy, thermal protection coating, ultra-high temperature materials and nuclear reactors, etc. This is mainly attributed to their excellent physical and chemical properties including high hardness, chemical inertness and superior electrochemical properties, etc. [1–5].

In recent years, many methods have been successfully used to prepare the high-entropy borides, including the direct synthesis by high-temperature treatment using metal diboride powders as raw materials [1,6], the borothermal reduction method [7] and boro/carbothermal reduction method from oxides materials [8–14], and self-propagating high-temperature synthesis from metal and B powders [15], molten salt synthesis method [16] and so on. Among these methods, the boro/carbothermal reduction method can realize the large-scale production of high entropy diboride powders, which has been verified in preparing single phase diboride powders [17,18]. Liu et al. [11] used this method to successfully prepare high entropy diboride (Hf0.25Ta0.25Nb0.25Ti0.25)B2 powders. However, lower temperature below than 2073 K led to the incompletion of boro/carbothermal reduction process, not forming the single phase high-entropy boride powders. High temperature of 2073 K was needed to realize the pure high-entropy boride powders on the condition of excess 40 wt% B4C in raw powders, and the average particle size was 260 nm. As is known that high-temperature condition easily causes the formation of coarse grains, which goes against the densification and the improvement of properties in sintering process of high-entropy powders [19]. Therefore, the preparation of high-entropy boride powders with fine grain size at lower temperature is crucial. High-energy ball milling process can realize the powders to the nanoscale in powder processing, which offers the opportunities to increase the reaction kinetics of powders [20,21]. This refinement process can realize the synthesis of fine high-entropy boride powders, which has been successfully used to synthesize fine ZrB2 powders [22,23]. Nowadays, the research about the preparation of high-entropy boride powders via a simple high-energy ball milling process-assisted boro/carbothermal reduction is still rarely. Meanwhile, owing to the big compositional design space brought by the complexity and multifomity of transition metal elements, the researches about the synthesis of new kind of high-entropy diboride ceramics are still insufficient and need to further be extended.

Therefore, in this paper, (W0.2V0.2Ta0.2Nb0.2Ti0.2)B2 (HEB) powders were successfully prepared by the high-energy ball milling (HEBM) assisted boro/carbothermal reduction method. The thermodynamic behavior of...
HEB precursor was analyzed by the thermodynamic calculations and TG-DSC process. The effects of the heating temperature and B₄C content on the formation of as-prepared HEB powders were analyzed. The morphology and structure of as-prepared HEB powders were studied. Furthermore, the formation mechanism of as-prepared HEB powders was discussed. The purpose of this study was to provide a vital step for the commercialization of high-entropy boride powders.

2. Experimental

2.1. Synthesis of high-entropy boride powders

In this research, commercially available WO₃ powders (AR, purity: 99.8 wt %), V₂O₅ powders (AR, purity: 99 wt %), Ta₂O₅ powders (AR, purity: 99.9%), TiO₂ powders (AR, purity: 99 wt %) and Nb₂O₅ powders (AR, purity: 99.9 wt %) were all from Shandong West Chemical Industry Co. Ltd. B₄C powders (purity: 99.9 wt %) and carbon black powders (purity: 99 wt %) were from Shanghai Shuitian Material Technology Co., Ltd. The detail procedures were described as follows: The weighted WO₃, V₂O₅, Ta₂O₅, TiO₂, Nb₂O₅, B₄C and C were milled for 2 h by a HEBM method using WC balls as the medium. The material of the ball-mill pot was also WC. The stoichiometric molar ratio of WO₃/V₂O₅/Ta₂O₅/TiO₂/Nb₂O₅/B₄C/C was 2:1:2:1:5:20. To compensate the loss of B, the precursors with different excess B₄C (5 wt% and 10 wt. %) were also prepared. After milling, the obtained precursors were heated to 1200 ~ 1600°C at a rate of 10°C/min and processed 2 h. An argon gas atmosphere (99.99%, purity) was used to prevent oxidation during the whole heating and cooling processes.

2.2. Characterization

The thermal behavior of HEB precursor was studied by TG-DSC equipment (STA449F3, NETZSCH-Gerätebau GmbH, German). The phase composition of HEB precursor and as-prepared HEB powders was characterized using X-ray diffraction (XRD, D/max-2550VB+/PC, Japan). The morphologies and structure of HEB precursor and as-prepared HEB powders were analyzed by a scanning electron microscope (FESEM, S-4700, Hitachi, Tokyo, Japan) and a transition electron microscope (TEM, Tecnai F-20, FEI, Hillsboro, OR) with energy-dispersive X-ray analyzer system. The particle size distributions of HEB precursor and as-prepared HEB powders were statistically measured from about 200 grains.

3. Results and discussion

3.1. Characterization of HEB precursor

XRD pattern and SEM image of HEB precursor powders prepared by HEBM are shown in Figure 1. Five metal oxides, B₄C and C phase, are observed in Figure 1(a). Due to the HEBM process, the particles of the original powder appear nano-sized, which will cause the diffraction peaks to be significantly broadened. To confirm this speculation, SEM image and the particle size distribution of the as-prepared HEB precursor powders after HEBM are given in Figure 1(b). It is found that the HEB precursor powders are spherical, with fine and good dispersibility. The particle size of HEB precursor powders is mainly concentrated at 100 ~ 300 nm, and its D₅₀ is 199 nm, which is consistent with the SEM results. It is worth noting that about 1μm of soft agglomerates are also observed in the SEM results.

3.2. Preparation of HEB powders

Figure 2 shows the TG-DTG-DSC curves of prepared HEB precursor powders. It is evidently seen that the TG curve almost shows no weight loss before 1100°C, meanwhile, no strong endothermic or exothermic peaks can be observed in DSC curve, which indicates that no reduction reaction has occurred. A slight weight loss is observed above 1100°C, as the release of gaseous product. As the temperature increases, the rate of weightlessness increases, as shown by the DTG

Figure 1. XRD patterns (a); SEM image and particle size distribution (b) of HEB precursor.
curve, reaching a maximum at 1400°C. Additionally, a strong endothermic peak at 1400°C can be evidently observed in the DSC curve, attributing to the boro/carbothermal reaction of oxides. The flat TG curve indicates the almost completeness of boro/carbothermal reaction process of precursor. It is obtained that the ceramic yield is 54% at 1500°C. Moreover, a huge endothermic range exists at around 1400°C, which is believed to be the solid solution process of the obtained powders.

Figure 3 shows the phase evolution of HEB precursor at different temperatures for 2 h. When the mixed powders are prepared based on the stoichiometric ratio, the XRD of obtained HEB powder is all composed of a dominant (W_{0.2}V_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2 (AlB_2 prototype, space group P6/mmm, no. 191) phase and minor (W_{0.2}M_{1-x})B (CrB prototype, space group Cmcm, no. 63) solid solution phase, meaning that the solid solution process is incomplete at 1500°C and 1600°C [24–28]. On the one hand, the formation of (W_{0.2}M_{1-x})B solid solution phase may be caused by insufficient B source under the stoichiometric ratio of the raw materials [29,30]. Usually, a small amount of B_2O_3 is found on the surface of B_4C, which has a higher vapor pressure at high temperature. Additionally, influence of O_2 impurity in Argon as well as diffused through the corundum furnace tube on the amount of B_4C cannot be ignored [13]. On the other hand, Qin [24] et al. found the dissolution and stability of soft WB_2 phase in high-entropy ceramics, the formation of (W_{0.2}M_{1-x})B solid solution phase could be explained via the formation enthalpies between AlB_2-type and CrB-type structures. The formation enthalpies (H_{WB} – H_{WB2}) are −0.277, −0.07 and −0.163 in eV/atom, for N = W, Nb and Ta, from the Material Project Database [31]. It can explain why the monoboride phase observed in HEB is (W_{0.2}M_{1-x})B. Finally, although having the similar XRD patterns at 1500°C to 1600°C, combined with the DSC curve results, it is more appropriate to choose 1600°C to obtain the solid solution phase owing to that higher temperature offers bigger reaction energy for the formation of single-phase solid solution.

To avoid the formation of (W_{0.2}M_{1-x})B solid solution phase, the HEB powders are further prepared at 1600°C by using excess amount of B_4C. The XRD results of obtained HEB powders are shown in Figure 4. Obviously, with increase of B_4C amount, the diffraction peaks of (W_{0.2}M_{1-x})B solid solution phase gradually decreases. (W_{0.2}M_{1-x})B solid solution phase disappears when the excess amount of B_4C is 10 wt.% indicating that excess amount of B_4C accelerates the conversion of (W_{0.2}M_{1-x})B solid solution. Furthermore, Table 1 lists the lattice parameters of single phase diboride and HEB. It can be clearly seen that the lattice parameters of HEB are almost equal to the average value of five individual borides, which further proves that the as-obtained powders are (W_{0.2}V_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B_2.

Figure 4. XRD patterns of powders obtained under different M/ B_4C molar ratios 1600°C.

| Sample | TaB_2 | TiB_2 | W_2B_6 | NbB_2 | VB_2 | Average | HEB-1 |
|--------|-------|-------|--------|-------|-------|---------|-------|
| a (Å)  | 3.076 | 3.028 | 3.023  | 3.172 | 2.993 | 3.046   | 3.049 |
| c (Å)  | 3.265 | 3.228 | 3.057  | 3.274 | 3.028 | 3.170   | 3.210 |
Figure 5 shows the SEM image and particle size distribution of HEB powders prepared with excess 10 wt% B₄C at 1600°C for 2 h. Figure 5(a) shows that obtained products have sphere-like particles and the particles are uniform and fine. Furthermore, the particle size distribution is shown in Figure 5(b), and the D₅₀ is about 151 nm. By comparison, it is found that the particle size is reduced from 199 nm of HEB precursor to 151 nm of the as-obtained HEB powders, indicating that the boro/carbothermal reduction decreases can reduce the particle size of HEB powders. Additionally, it is seen that some weak sintering necks have been formed between the high entropy diboride particles, indicating that the as-obtained products have higher sintering activity.

A representative TEM morphology of as-synthesized HEB powders with excess 10 wt.% B₄C content synthesized at 1600°C is shown in Figure 6(a). The HEB powders show near-spherical shape and their average particle size (measured by 50 particles sizes) is ~151 nm, which has been confirmed in SEM image. Meanwhile, an amorphous layer (B₂O₃) with ~2 nm is observed on the HEB powder surface. The EDS compositional maps of as-obtained HEB powders are also given. Ta, Nb, Ti, W and V elements are shown that the highly uniform distribution without element agglomeration is scanned in as-obtained HEB powders, further confirming that as-synthesized products are composed of (W₀.2V₀.2Ta₀.2Nb₀.2Ti₀.2)B₂.

3.3. Formation mechanism of HEB powders

The thermodynamic calculations are used to analyze the synthesis possibility of HEB powders. The Gibbs free energy change (ΔG°ₐₜ) of the possible chemical reactions is conducted by using HSC 6.0 (a software to calculate the Gibbs free energy change, produced by the Metso Outotec Finland Oy). According to the raw materials, the possible reactions and the relationship between ΔG°ₐₜ and temperature are as follows:

\[ \text{WO}_3 + 1/2\text{B}_4\text{C} + 5/2\text{C} = \text{WB}_2 + 3\text{CO}(g) \]  \hspace{1cm} (1)

\[ \Delta G°ₐₜ = 265242 - 506.2T + RT \ln \left( \frac{\text{CO}}{\text{P}_{\text{CO}}} \right)^3 \text{ (J/mol)} \]

\[ 1/2\text{V}_2\text{O}_5 + 1/2\text{B}_4\text{C} + 2\text{C} = \text{VB}_2 + 5/2\text{CO}(g) \]  \hspace{1cm} (2)

Figure 6. TEM (a); HRTEM (b) and EDS compositional maps of as-obtained HEB powders obtained at 1600°C with excess 10 wt% B₄C.
\[ \Delta G_{R,T}^0 = 302616 - 395.1T + RT \cdot \ln \left( \frac{P_{CO}}{P_0} \right)^2 \ (J/mol) \]  
(3) 

\[ \Delta G_{R,T}^0 = 556034 - 420.5T + RT \cdot \ln \left( \frac{P_{CO}}{P_0} \right)^2 \ (J/mol) \]  
(4) 

\[ \Delta G_{R,T}^0 = 466352 - 335.6T + RT \cdot \ln \left( \frac{P_{CO}}{P_0} \right)^2 \ (J/mol) \]  
(5) 

\[ \Delta G_{R,T}^0 = 519472 - 421.4T + RT \cdot \ln \left( \frac{P_{CO}}{P_0} \right)^2 \ (J/mol) + 1/5TB_2 + 1/5NbB_2 \]  
(6) 

\[ \Delta G_{R,T}^0 = \Delta G_{M}^0(1/mol)1/5WO_3 + 1/10TaO_3 + 1/10TiO_2 \]  
(7) 

\[ \Delta G_{R,T}^0 = 421943 - 415.8T + \Delta G_{M}^0 + RT \cdot \ln \left( \frac{P_{CO}}{P_0} \right)^2 \ (J/mol) \]  
(8) 

where \( \Delta G_{M}^0 \) actually stands for mixing Gibbs free energy change of HEB powder. Assuming that HEB powder is the ideal Raoultian solution, \( \Delta G_{M}^0 \) can be calculated by the Equation (8).

\[ \Delta S_{min} = T \Delta S_{min} \]

Where \( \Delta S_{min} \) actually stands for mixing entropy of HEB powders, which is expressed based on the following equation [3,14]:

\[ \Delta S_{min} = \frac{R}{3} \sum_{i=1}^{N} x_i \ln x_i \]

(9) 

Where ideal gas constant \( R \) is 8.314, metal element species \( N \) is 5, and molar fraction of the \( i \)th metal element in sublattice is \( x_i \). From Equations (8) and (9), \( \Delta G_{R,T}^0 \) is calculated to be \(-4.5 \ T\). Therefore, the mathematically expressed of \( \Delta G_{R,T}^0 \) from reaction (7) can be shown as:

\[ \Delta G_{R,T}^0 = 421943 - 420.3T + RT \cdot \ln \left( \frac{P_{CO}}{P_0} \right)^2 \ (J/mol) \]

(10) 

The system may maintain a standard pressure due to the flowing Argon gas. The unknown reaction rate of chemical reactions makes it difficult to precisely evaluate or measure the partial pressure of CO gaseous product in the system [11]. As stated in other reports, assume that the partial pressure of CO is equal to the standard pressure [32]. Figure 7 shows the \( \Delta G_{R,T}^0 \) of those possible reactions. It can be observed that \( \Delta G_{R,T}^0 \) of all reactions is negative (\( T > 1400 \ K \)) indicating that they all proceed spontaneously. However, it can be seen that due to its very negative \( \Delta G_{R,T}^0 \) compared to reaction 6, the reaction 7 is prone to generate HEB. In short, it is possible to obtain HEB by reaction 6 from the thermodynamic aspect.

Figure 7. Gibbs free energy change of reactions at different temperatures.

To clearly understand the formation process of HEB powders, Figure 8 shows the phase evolution of excess 10 wt.% \( B_2C \) precursor at different temperatures for 2 h. At 1200°C, unreacted oxides, newly formed borides and oxide solid solutions are observed. In addition, obvious diffraction peaks of TMC (the transition metal carbide, \( TM = W, V, Ta, Ti, Nb \)) phase can be observed in samples obtained at 1200–1400°C. This indicated that in addition to reactions (1–7), the other reactions may also occur [11].

Figure 8. Phase evolution of HEB precursor at different temperatures for 2 h.
Table 2. Lattice parameters in peak indices for the as-synthesized HEB products at different temperatures.

| Lattice parameters | HEB-1400°C | HEB-1500°C | HEB-1600°C | Average |
|--------------------|------------|------------|------------|---------|
| a (Å)              | 3.082      | 3.058      | 3.052      | 3.049   |
| c (Å)              | 3.227      | 3.176      | 3.120      | 3.210   |

\[
\begin{align*}
\frac{1}{5}&\text{WO}_3+\frac{1}{10}\text{V}_2\text{O}_5+\frac{1}{10}\text{Ta}_2\text{O}_5+\frac{1}{5}\text{TiO}_2 \\
+\frac{1}{10}\text{Nb}_2\text{O}_5+\frac{1}{14}\text{B}_4\text{C} & = (\text{W}_2\text{V}_2\text{Ta}_2\text{Nb}_2\text{Ti}_2) \text{B} \\
2+4&\text{B}_2\text{O}_3+\frac{11}{14}\text{CO}(g) \quad \text{(12)}
\end{align*}
\]

where TMO are the five oxides of transition metals. Obviously, compared with the reaction (1–5), Equation (11) can consume much more amount of \( \text{B}_4\text{C} \). What is more, the by-product \( \text{B}_2\text{O}_3 \) has a high vapor pressure and thereby it will rapidly evaporate with flowing Ar gas [32,33], which can further accelerate the occurrence Equation (11) to consume much more amount of \( \text{B}_4\text{C} \). This explained the generation of TMC phase by the Equation (12). Compared with the diffraction peaks at 1300°C, diffraction peaks of TMC phase are significantly weakened at 1400°C, accompanied by the formation of TMB, indicating that the solid solution phase of borides in the sample begins to form. The wide diffraction peaks indicate that the solid solution process has not been completed at 1400°C, which is the superposition of multiple solid solution phase diffraction peaks (such as Ta-based and Nb-based solid solutions). In addition, in DSC curve, a strong endothermic peak observed at 1400°C means the formation of single-phase boride and main high entropy solid solution phase. When temperature is increased to 1500°C, HEB is the main phase, but traces of impurity peaks can also be observed, indicating that higher temperatures are required to stimulate the formation of high-entropy phase. The increasing temperature causes the transformation from solid solution of TMC to high-entropy diboride by accelerating the boron/carbothermal reduction reaction. The solid solution situation of the powders with the temperature is analyzed using unit cell parameters. The lattice parameter of the high-entropy phase is obtained by adding the unit cell parameter values of five single-phase borides and taking the average value. This value can be approximately regarded as the theoretical value of the high-entropy phase. This method has been adopted by many researchers, such as Liu et al. [3] and Feng et al. [13], contributing to analyze the solid solution process. Finally, JADE is used to calculate the unit cell parameters of the products obtained at different temperatures. The data are shown in Table 2. According to the calculation results, the unit cell parameter \( a \) of the high-entropy phase gradually decreases with increasing temperature, and the value of \( c \) becomes larger due to the solid solution of \( \text{W} \) at 1600°C. At 1600 degrees, the values of \( a \) and \( c \) are close to the theoretically calculated values, further confirming pure HEB can be obtained at 1600°C.

4. Conclusion

Single-phase and fine high-entropy boride (HEB) powders were obtained by a simple and easy HEBM assisted boro/carbothermal reduction method. Results showed that the temperature and B source contents played a key role in the synthesis of purity HEB powders. When excess 10 wt.% \( \text{B}_4\text{C} \) was introduced, the single-phase HEB powders were synthesized at 1600°C, and it showed the hexagonal crystal structure of metal diborides. The particle size was reduced from 199 nm of HEB precursor to 151 nm of the as-obtained HEB powders by the boro/carbothermal reduction. Meanwhile, the HEB powder had a compositional uniformity of \( \text{W} \), \( \text{V} \), \( \text{Ta} \), \( \text{Ti} \), \( \text{Nb} \) and \( \text{B} \) elements, which was confirmed by EDS analysis using the TEM. Through discussing the thermodynamics process related to these possible chemical reactions and combining the XRD results at different temperatures, it was obtained that higher temperature and enough B source were required to stimulate the formation of high-entropy phase. This work will be a vital step for the commercialization of high-entropy boride powders.

Acknowledgments

The authors acknowledge the support from the National Natural Science Foundation of China (51804202), the Natural Science Foundation of Hebei Province (E2019210042, E2019210295), Natural Science Foundation of the Hebei Education Department (QN2018043, QN2019137) and Opening Foundation of Sichuan Province Engineering Center for Powder Metallurgy (SC-FMYJ2018-08).

Disclosure statement

No potential conflict of interest was reported by the author(s).

References

[1] Gild J, Zhang YY, Harrington TJ, et al. High-entropy metal diborides: a new class of high entropy materials and a new type of ultrahigh temperature ceramics. Sci Rep. 2016;6:37946.
[2] Wang YP, Gan GY, Wang W, et al. Ab Initio prediction of mechanical and electronic properties of ultrahigh temperature high-entropy ceramics (\( \text{Hf}_2\text{Zr}_2\text{Ta}_2\text{Mo}_2\text{Ti}_2\text{B}_2 \) \( M = \text{Nb}, \text{Mo}, \text{Cr} \)). Phys Status Solidi. 2018;255:1800011.
[3] Liu D, Wen TQ, Ye BL, et al. Synthesis of superfine high-entropy metal diboride powders. Scripta Mater. 2019;167:110–114.

[4] Tallarita G, Licheri R, Garroni S, et al. Novel processing route for the fabrication of bulk high-entropy metal diborides. Scripta Mater. 2019;158:100–104.

[5] Monteverde F, Saraga F, Gaboardi M. Compositional disorder and sintering of entropy stability (Hf,Nb,Ta,Ti,Zr)B solid solution powders. J Eur Ceram Soc. 2020;40(12):3807–3814.

[6] Failla S, Galizia P, Fu S, et al. Formation of high entropy metal diborides using arc-melting and combinatorial approach to study quinary and quaternary solid solutions. J Eur Ceram Soc. 2020;40:588–593.

[7] Zhang Y, Guo WM, Jiang ZB, et al. Dense high-entropy boride ceramics with ultra-high hardness. Scripta Mater. 2019;164:135–139.

[8] Gu JF, Zou J, Sun SK, et al. Dense and pure high-entropy metal diboride ceramics sintered from self-synthesized powders via boro/carbothermal reduction approach. Sci China Mater. 2019;62:1898–1909.

[9] Monteverde F, Saraga F. Entropy stabilized single-phase (Hf,Nb,Ta,Ti,Zr)B solid solution powders obtained via carbo/boro-thermal reduction. J Alloy Compd. 2020;824:153930.

[10] Gild J, Wright A, Quiambao-Tomko K, et al. Thermal conductivity and hardness of three single-phase high-entropy metal diborides fabricated by boro-carbothermal reduction and spark plasma sintering. Ceram Int. 2020;46:6906–6913.

[11] Liu D, Liu HH, Ning SS, et al. Synthesis of high-purity high-entropy metal diboride powders by boro-carbothermal reduction. J Am Ceram Soc. 2019;102:7071–7076.

[12] Zhang Y, Jiang ZB, Sun SK, et al. Microstructure and mechanical properties of high-entropy borides derived from boro/carbothermal reduction. J Eur Ceram Soc. 2019;39:3920–3924.

[13] Feng L, Fahrenholtz WG, Hilmas GE. Two-step synthesis process for high-entropy diboride powders. J Am Ceram Soc. 2020;103:724–730.

[14] Liu JX, Shen XQ, Wu Y, et al. Mechanical properties of hot-pressed high-entropy diboride-based ceramics. J Adv Ceram. 2020;9(3):503–510.

[15] Tallarita G, Licheri R, Garroni S, et al. High-entropy transition metal diborides by reactive and non-reactive spark plasma sintering: a comparative investigation. J Eur Ceram Soc. 2020;40:942–952.

[16] Liu D, Liu HH, Ning SS, et al. Chrysanthemum-like high-entropy diboride nanoflowers: a new class of high-entropy nanomaterials. J Adv Ceram. 2020;9:339–348.

[17] Qiu HY, Guo WM, Zou J, et al. ZrB2 powders prepared by boro/carbothermal reduction of ZrO2: the effects of carbon source and reaction atmosphere. Powder Tech. 2012;217:462–466.

[18] Deng XG, Du S, Zhang HJ, et al. Preparation and characterization of ZrB2-SiC composite powders from zircon via microwave-assisted boro/carbothermal reduction. Ceram Int. 2015;41:14419–14426.

[19] Baumgartner HR, Steiger RA. Sintering and properties of titanium diboride made from powder synthesized in a plasma-arc heater. J Am Ceram Soc. 1984;67(3):207–212.

[20] Suryanarayana C. Mechanical alloying and milling. Prog Mater Sci. 2001;46(1–2):11–84.

[21] Zamora V, Ortiz AL, Guiberteau F, et al. Crystal-size dependence of the spark-plasma-sintering kinetics of ZrB2 ultra-high-temperature ceramics. J Eur Ceram Soc. 2012;32(2):271–276.

[22] Zamora V, Ortiz AL, Guiberteau F, et al. On the crystal-lattice size refinement of ZrB2 by high-energy ball-milling in the presence of SiC. J Eur Ceram Soc. 2011;31:2407–2414.

[23] Zamora V, Ortiz AL, Guiberteau F, et al. In situ forma tion of ZrB2-ZrO2 ultra-high-temperature ceramic composites from high-energy ball-milled ZrB2 powders. J Alloy Compd. 2012;518:38–43.

[24] Qin MD, Gild J, Wang HR, et al. Dissolving and stabilizing soft WB2 and MoB2 phases into high-entropy borides via boron-metals reactive sintering to attain higher hardness. J Eur Ceram Soc. 2020;40:4348–4353.

[25] Shibuya M, Kawata M, Ohyanagi M, et al. Titanium diboride–tungsten diboride solid solutions formed by induction-field-activated combustion synthesis. J Am Ceram Soc. 2003;86:706–710.

[26] Shibuya M, Yamamoto Y, Ohyanagi M. Simultaneous densification and phase decomposition of TiB2-WB2 solid solutions activated by cobalt boride addition. J Eur Ceram Soc. 2007;27:307–312.

[27] Jiang C, Pei Z, Liu Y, et al. Preparation and characterization of superhard AlB2-type WB2 nanocomposite coatings. Phys Status Solidi A. 2013;210:1221–1227.

[28] Shen XQ, Liu JX, Li F, et al. Preparation and characterization of diboride-based high entropy (Ti0.2Zr0.8Hf0.2Nb0.2Ta0.8)B2-SiC particulate composites. Ceram Int. 2019;45:24508–24514.

[29] Fahrenholtz WG, Binner J, Zou J. Synthesis of ultra-refractory transition metal diboride compounds. J Mater Res. 2016;31:2757–2772.

[30] Wang HL, Lee SH, Kim HD. Nano-hafnium diboride powders synthesized using a spark plasma sintering apparatus. J Am Ceram Soc. 2012;95:1493–1496.

[31] Jain A, Ong SP, Hautier G, et al. Commentary: the Materials Project: a materials genome approach to accelerating materials innovation. APL Mater. 2013;1:011002.

[32] Feng L, Fahrenholtz W, Hilmas G, et al. Synthesis of single phase high-entropy carbide powders. Scripta Mater. 2019;162:90–93.

[33] Parthasarathy TA, Rapp RA, Opeka M, et al. A model for the oxidation of ZrB2, HfB2 and TiB2. Acta Mater. 2007;55:5999–6010.