

# Synthesis of $W_2B_5$ powders by the reaction between $WO_3$ and amorphous B in NaCl/KCl flux



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## ABSTRACT

$W_2B_5$  powder was synthesized by the reaction between  $WO_3$  and amorphous B in NaCl/KCl flux. The results indicate that appropriate amount of NaCl/KCl flux significantly improved the completion of borothermal reduction reaction. When the weight of NaCl/KCl was 10 times that of  $WO_3/B$ , pure phase  $W_2B_5$  powder could be obtained at 1100 °C. The synthesized powder was composed of agglomerated nanosized particles. The oxidation resistance of the synthesized  $W_2B_5$  powder was evaluated by a simultaneous thermogravimetric and differential scanning calorimetry technique.

## 1. Introduction

Transition metal borides are a class of refractory materials with excellent structural and functional characteristics, such as high melting point, high strength and hardness, outstanding thermal shock & oxidation resistance, and good electrical & thermal conductivity [1,2]. These properties made transition metal borides candidate materials for refractory crucibles in the field of smelting, superhard and wear-resistant parts in structural units, thermal protection components in aerospace, and electrodes at high temperature [1,2].

Recently,  $W_2B_5$  attracts many attentions in the field of structural ceramic composites [3–7].  $B_4C-W_2B_5$  composite with 5 vol% graphite was reported to have both high hardness (30.2 GPa) and high fracture toughness (11.9 MPa  $m^{1/2}$ ) [3].  $C/W_2B_5$  composites achieved high flexural strengths of around 800 MPa and high fracture toughness above 8.0 MPa  $m^{1/2}$  with a rather low electrical resistivity of about  $6.0 \times 10^{-4} \Omega \cdot m$  [5]. Due to the absence of commercial  $W_2B_5$  powder,  $W_2B_5$  phases in the ceramic composites were mostly in situ synthesized during the sintering process [3–7]. Therefore, the synthesis of highly pure  $W_2B_5$  powders is quite important for its application in the field of composites.

Among the large family of transition metal borides, pure tungsten borides are more difficult to be synthesized because there are at least seven compounds in W–B system:  $W_2B$ ,  $\alpha$ -WB,  $\beta$ -WB,  $W_2B_5$ ,  $WB_2$ ,  $WB_4$  and  $WB_{12}$  [8]. At present, various tungsten boride powders and bulks

have been prepared by different methods [9–21]. Normally, tungsten borides were prepared by three routes: (1) direct reaction between elemental W and B, (2) magnesiothermic reduction of tungsten oxides and  $B_2O_3$ , and (3) borothermal reduction of tungsten oxides by B. Tungsten borides prepared by route (1) normally have high purity but the raw materials are costly. For example,  $WB_4$  bulks were prepared by arc melting of elemental W and amorphous B mixtures at ambient pressure, and their Vickers hardness were as high as 43.3 GPa [11,12]. Route (2) uses cheap raw materials but the reaction is difficult to be controlled because a self-propagating high-temperature reaction is ignited during the synthesis process [18,20]. As a result, the reaction is normally incomplete and impurities are present in the final product. In addition, in order to dissolve MgO, leaching process is unavoidable, which consumes acid and causes problems such as safety and environmental pollution. Derin B. et al. synthesized  $W_2B_5$  powders by reaction (2), the purity of  $W_2B_5$  phase could be enhanced from 72.6% to 98.2% by a second self-propagation high-temperature synthesis (SHS) and leaching process [20]. Pure  $W_2B_5$  powders were successfully synthesized via mechanochemical reduction of  $WO_{2.72}$  and  $B_2O_3$  by elemental Mg at room temperature, but the mechanochemical alloy process was as long as 30 h [19]. Route (3) is a simple solid-state reaction but the synthesis temperature is high. Peshev P. et al. synthesized  $W_2B_5$  powders by the reaction of  $WO_2$  and elemental B in vacuum. It was found that  $W_2B_5$  phase appeared above 1300 °C and pure  $W_2B_5$  phase with a deficient amount of boron could only be obtained at 1600 °C

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[21].

Herein, we report the synthesis of  $W_2B_5$  powders by a borothermal reduction reaction between  $WO_3$  and amorphous B in NaCl/KCl flux. Compared with traditional borothermal reduction [21], in this paper, cheaper  $WO_3$  replaced  $WO_2$  as a raw material, and the introduction of NaCl/KCl flux during the heating process greatly decreased the synthesis temperature from 1600 °C to 1100 °C. The antioxidant property of the as-synthesized  $W_2B_5$  powder was also investigated by a simultaneous thermogravimetric analysis and differential scanning calorimeters (TG-DSC) technique.

## 2. Experimental procedures

Tungsten trioxide ( $WO_3$ , > 99% purity), amorphous boron (B, 95.82% purity,  $Mg \leq 2$  wt%, hydrogen peroxide insoluble substances  $\leq 1.0$  wt%, water soluble boron  $\leq 0.5$  wt%,  $H_2O \leq 0.5$  wt%,  $d_{50} \leq 0.90$   $\mu m$ ), sodium chloride (NaCl, A.R.) and potassium chloride (KCl, A.R.) powders were used as starting materials. The above powders were mixed uniformly by hand with an agate mortar and pestle. The molar ratio of  $WO_3$  and B was set as 2:9 according to reaction (1) and the mass of the theoretical target product for each experiment is 0.5 g. NaCl/KCl mixture with a 50 mol% NaCl has the lowest eutectic point of 658 °C in the NaCl–KCl system, which served as flux during the synthesis process. In order to study the effects of flux on the phase compositions of the samples, different amount of NaCl/KCl mixture was added to the  $WO_3$ /B reactants. The weight ratio of flux salts and reactants was represented by R with values of 0, 5, 10 and 15. The powder mixture was poured into a corundum crucible which was put in the middle of a corundum tube for heating at 900–1100 °C for 1 h. The heating rate was kept as 10 °C/min for the whole temperature ramping process. As the furnace temperature naturally decreased below 60 °C, the crucible was taken out. In order to prevent oxidation of raw B powder and boride product, the whole temperature ramping and falling process was protected by the flowing argon gas. NaCl/KCl were not involved in the reaction and therefore remained in the product.  $B_2O_3$  was the byproduct of the reaction, which could be dissolved by hot water [22–24]. After immersing, filtrating, washing and drying, the synthesized  $W_2B_5$  powders were obtained.



Phases of the sample were characterized by powder X-ray diffraction (XRD, Ultima IV, Rigaku Co., Japan) with Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å). Morphology of the product was observed with a field scanning electron microscope (FSEM, S4800, Hitachi, Tokyo, Japan). Microstructural analyses of the product were performed on a transmission electron microscopy (TEM, JEM2100, JEOL, Tokyo, Japan) with selected-area electron diffraction (SAED). Simultaneous thermogravimetric analysis and differential scanning calorimeters (TG-DSC, Netzsch STA 449F3, Netzsch Geratebau GmbH, Germany) was used to study the oxidation resistance of the product. TG-DSC experiment was performed in air at 20–1300 °C with a heating rate of 10 °C/min.

## 3. Results and discussion

$W_2B_5$  powders were firstly synthesized via traditional borothermal reduction, where only  $WO_3$  and B powders were used as reactants and no flux was added during the reaction process. Fig. 1 shows XRD patterns of products obtained at 900–1100 °C. As seen in Fig. 1(a), the product was WB phase with a trace of metal W and unreacted  $WO_3$  at a synthesis temperature of 900 °C. When the synthesis temperature was enhanced to 1000 °C,  $W_2B_5$  phase appeared (Fig. 1(b)). At 1100 °C,  $WO_3$  phase disappeared and  $W_2B_5$  replaced WB as the main crystalline phase (Fig. 1(c)). The above results indicated that  $WO_3$  was firstly reduced to W or WB and then to  $W_2B_5$ . Considering the volatility of  $WO_3$  at temperature above 800 °C [21], further increasing temperature was not

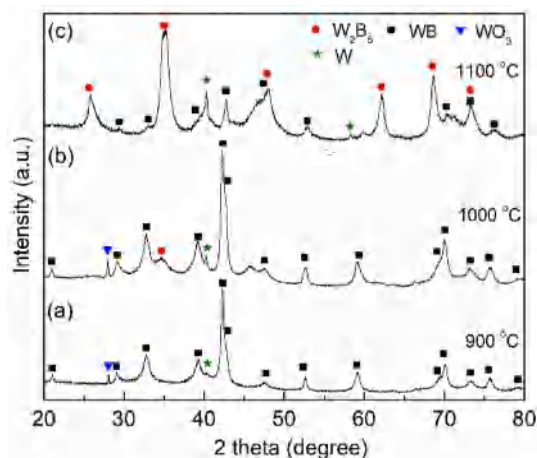


Fig. 1. XRD patterns of products synthesized via traditional borothermal reduction at (a) 900 °C, (b) 1000 °C and (c) 1100 °C.

beneficial for the synthesis of pure  $W_2B_5$  due to the excess of B. Peshev P. et al. synthesized  $W_2B_5$  powders by the reaction of  $WO_2$  and elemental B in vacuum. The reduction process was different from this study [21]. According to the report,  $WO_2$  was still the only crystal phase at 1000 °C.  $W_2B$  phase, instead of WB or W, firstly appeared at 1100 °C and  $W_2B_5$  phase appeared above 1300 °C.

Fig. 2 presents XRD patterns of products synthesized by borothermal reduction in NaCl/KCl flux at 900–1100 °C with  $R = 10$ . According to Fig. 2(a), most of  $WO_3$  was firstly reduced to WB at 900 °C, which was similar to Fig. 1(a). The XRD peaks for WB in Fig. 2(a) are wider than those in Fig. 1(a), revealing that the presence of flux greatly decreased the particle size and crystallinity of WB powder. In this situation, the NaCl/KCl flux served as a dilute agent. When the synthesis temperature increased to 1000 °C,  $W_2B_5$  phase was already the main crystalline phase (Fig. 2(b)). Pure phase  $W_2B_5$  powder was obtained at 1100 °C (Fig. 2(b)). When Fig. 2(b and c) was compared with Fig. 1(b and c), it revealed that the introduction of NaCl/KCl flux promoted the reaction process of borothermal reduction [22–24]. Theoretically, magnesium and hydrogen peroxide insoluble substances will remain in the final product and affect its purity. However, the amount of the impurities in the final product is below the detection limit of XRD. Considering the fact that it is still a challenge to synthesize phase pure tungsten boride powders based on XRD, the influence of the impurities in the raw amorphous boron on the final product could be ignored.

The borothermal reduction of  $WO_3$  is a strongly exothermic

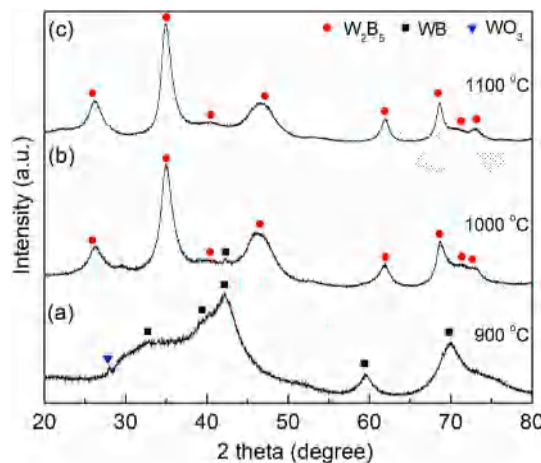
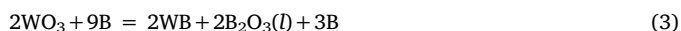


Fig. 2. XRD patterns of products synthesized via borothermal reduction in NaCl/KCl flux at (a) 900 °C, (b) 1000 °C and (c) 1100 °C with  $R = 10$ .

reaction, which is much more exothermic than the reaction between W and B [16]. The adiabatic temperature calculated from the enthalpy of formation of  $W_2B_5$  at 25 °C was 2369.8 °C for the borothermal reduction (reaction (1)) and 1222.5 °C for the elemental reaction (reaction (2)), respectively. Considering that the product of borothermal reduction of  $WO_3$  at 900 °C was mainly WB (Fig. 1(a)), the adiabatic temperature was calculated according to reaction (3) and resulted value was 2074.8 °C. Generally, SHS reaction will occur when the adiabatic temperature is higher than 1500 °C [25]. Therefore, during the process of borothermal reduction, SHS might be activated to produce WB phase firstly. Then, WB continued to react with B to generate  $W_2B_5$ . Both WB and B are solid reactants and diffuse slowly between them. As a result, pure  $W_2B_5$  phase is difficult to be prepared by the direct reaction between  $WO_3$  and B with a stoichiometric ratio. The synthesis temperature was high and impurities and/or unreacted reactants were inevitable [16,21].



With the addition of NaCl/KCl flux during the borothermal reduction, NaCl/KCl served as a diluter and reduced the adiabatic temperature from 2369.8 °C ( $R = 0$ ) to 1361.3 °C ( $R = 5$ ) and 907.9 °C ( $R = 10$ ), respectively. In this situation, SHS could not be activated. Moreover, a liquid circumstance was provided and the mass transfer was accelerated by the convection and diffusion [26], which enabled reaction to be completed at low temperatures [22–24,27,28]. Actually, one of the resultants of borothermal reduction,  $B_2O_3$ , was liquid above 450 °C, but its amount was not enough to complete the reaction. To obtain pure phase  $W_2B_5$ , additional liquid phase was needed.

Fig. 3 shows the influence of flux amount on the XRD patterns of the products synthesized at 1100 °C. With no NaCl/KCl flux, i.e.  $R = 0$ , the obtained product contained a certain amount of WB and metal W, as indicated in Fig. 3(a). When the weight of flux was 5 times that of reactants, i.e.  $R = 5$ , only a trace of  $WO_3$  and WB is found in Fig. 3(b), indicating the beneficial effect of NaCl/KCl on the reaction. When  $R = 10$ , only target product  $W_2B_5$  phase is detected in Fig. 3(c) without any intermediate phase or unreacted reactant. When  $R = 15$ , WB phase appears in Fig. 3(d). The above results revealed that inappropriate amount of flux was unfavourable for the  $W_2B_5$  powder synthesis. Pure phase product could only be obtained by controlling the proper amount of flux. Comparing Fig. 3(a) with Fig. 3(b), it is found that all  $WO_3$  was consumed by reaction when  $R = 0$  but there was still a trace of  $WO_3$  remained in the product when  $R = 5$ , which could be explained as follows. The high adiabatic temperature indicated that SHS was easily

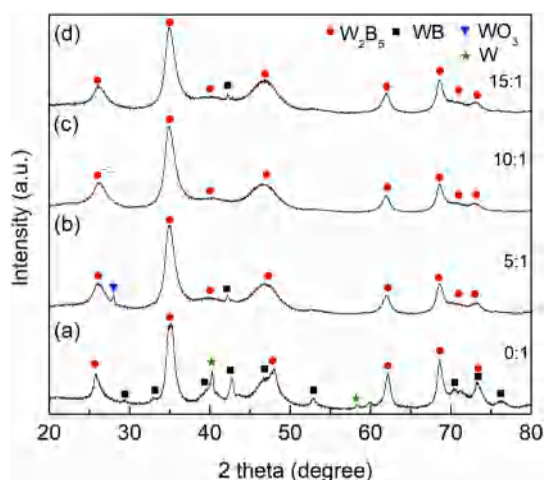


Fig. 3. XRD patterns of products synthesized via borothermal reduction in NaCl/KCl flux at 1100 °C with (a)  $R = 0$ , (b)  $R = 5$ , (c)  $R = 10$  and (d)  $R = 15$ .

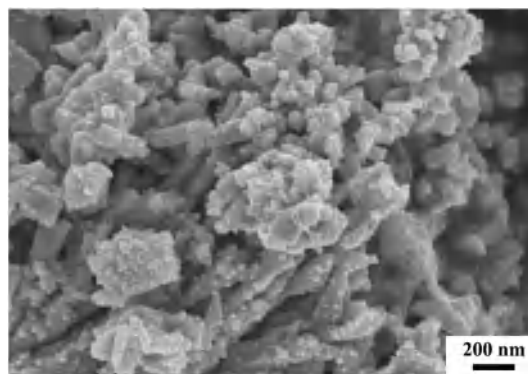
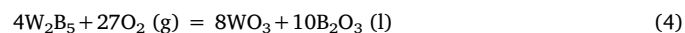


Fig. 4. SEM image of synthesized  $W_2B_5$  powder.

activated when  $R = 0$ . Because SHS completed at a very short time, it was very difficult to be controlled, which had no or less effect on the main product but the impurities or residual reactants in every experiment may not be the same. For example, both  $WO_3$  and W phase increases when the temperature increased from 900 °C to 1000 °C (Fig. 1). If SHS was not activated, the reaction was a slow solid-state reaction. When  $R \geq 5$ , the presence of flux accelerated the reaction and the phase composition of the product depended on temperature (Fig. 2) and  $R$  value (Fig. 3).

Fig. 4 shows the SEM image of product synthesized by borothermal reduction in NaCl/KCl flux at 1100 °C with  $R = 10$ , which was analysed to be pure  $W_2B_5$  phase by the XRD pattern in Fig. 2(c). SEM image indicated that the product was composed of agglomerated particles. TEM image in Fig. 5(a) revealed that the original particle size is nano-sized. The corresponding SAED pattern in Fig. 5(b) confirmed that the particles in Fig. 5(a) are polycrystalline. Several lattice fringes were clearly found in high-resolution TEM images, as indicated in Fig. 5(c) and (d). The calculated lattice fringe spacing was 0.17 nm, 0.19 nm, 0.23 nm, 0.25 nm and 0.26 nm, which corresponds to the d-spacing of (008), (105), (006), (101) and (100) crystal planes of hexagonal  $W_2B_5$  phase, respectively. The above result revealed that the particles were of  $W_2B_5$  phases.

The oxidation resistance of the synthesized  $W_2B_5$  powder was evaluated by simultaneous TG-DSC measurement, as shown in Fig. 6. During the heating process, there is 1.8% weight loss on the TG curve between 20 °C and 294 °C, which is due to the evaporation of water absorbed by the powder in air. After 294 °C, the TG curve ascends to 1134 °C with increasing temperature due to the oxidation of  $W_2B_5$  in the air. A significant exothermic peak appears at 454 °C on the DSC curve, corresponding to the maximum oxidation rate of  $W_2B_5$  powder. According to the differential thermal gravity (DTG) curve (not shown here), the maximum weight gain rate is at 456 °C. The above values show that the TG curve and the DSC curve have good consistency. Both  $WO_3$  and  $B_2O_3$  evaporate above 800 °C, resulting in weight loss, which decreases the weight gain induced by  $W_2B_5$  oxidation in air. From 800 °C to 1066 °C, the weight gain decreases and towards to zero with continuous exotherm. From 1066 °C to 1134 °C, the system gradually changes from exothermic to endothermic. When the temperature is above 1134 °C, the weight loses sharply, indicating the extensive evaporation of  $WO_3$  and  $B_2O_3$ . The weight gain between 294 °C and 1134 °C is 144.3%, less than the theoretical value (151.2%) calculated according to the reaction (4), which is resulted by the evaporation.



Because there are many compounds in W–B system, it is very difficult to synthesize pure phase tungsten boride powders. Table 1 summarizes the synthesis methods and the obtained products reported in the literatures. To obtain a single tungsten boride phase, B source (element B or  $B_2O_3$ ) was generally excessive [9–14,16–20]. Otherwise,

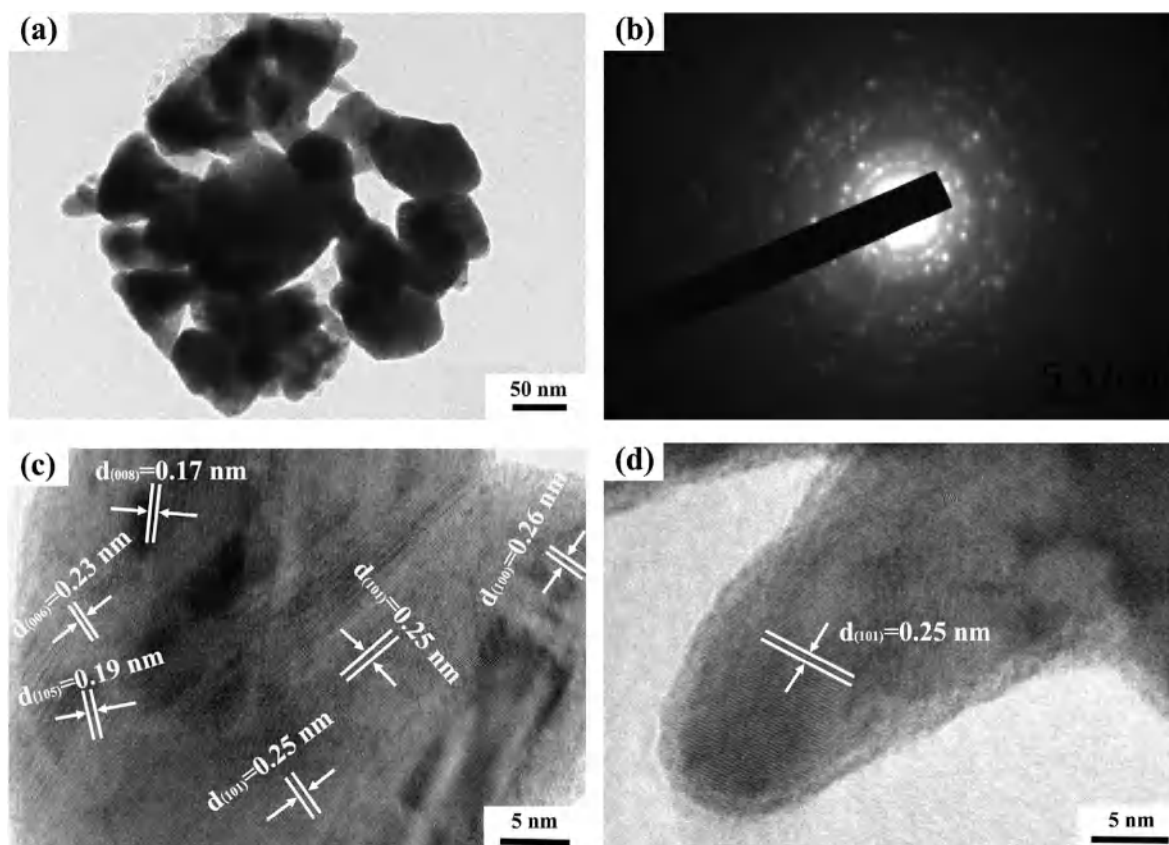


Fig. 5. (a) TEM, (b)SAED, (c) and (d) HRTEM image of synthesized  $W_2B_5$  powder.

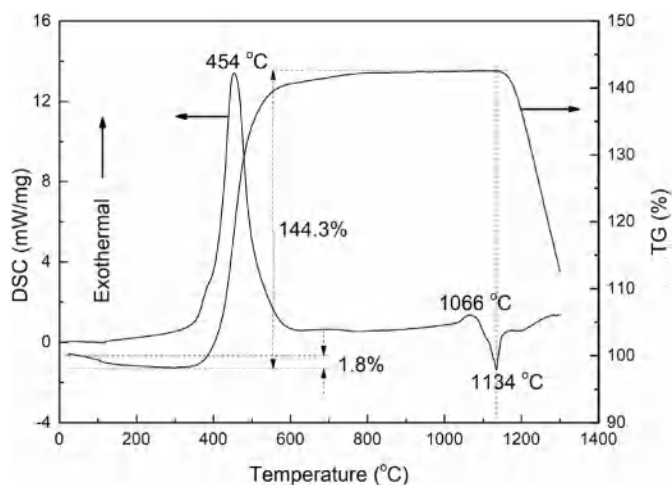


Fig. 6. TG-DSC curves of synthesized  $W_2B_5$  powder.

there were two or more tungsten borides in the product. The experiment on the reaction between elemental W and B at 1400 °C revealed that all borides formed only when the boron amount slightly exceeded their stoichiometric ratio [13].  $W_2B_5$  powder was reported to be successfully synthesized by firstly mechanical alloying of  $WO_{2.72}$ , Mg and 50% stoichiometrically excessive  $B_2O_3$  powders for 30 h and then HCl solution leaching [19]. The excessive  $B_2O_3$  not only ensured the completion of the reaction but also acted as a process control agent to prevent the crust formation during the mechanical alloying and mechanochemical process [19]. However, with the presence of NaCl/KCl flux,  $W_2B_5$  powder was successfully synthesized from the stoichiometric batch of elemental W and B [15]. In this study, similarly, only crystal  $W_2B_5$  phase was found in the XRD pattern (Fig. 2(c)) of the product

prepared from stoichiometric batch of  $WO_3$  and B according to reaction (1). The above results suggested that tungsten borides formation was promoted by the presence of flux. Strictly speaking, the evaporation of  $WO_3$  above 850 °C would result in B excess in this study. In order to evaluate the evaporation of  $WO_3$ , the synthesis experiment was performed with quartz tube. No deposit was found at outlet of the tube at 900 °C but white deposit appeared at 1000 °C and 1100 °C. In our previous report on  $NbB_2$  synthesis [24],  $B_2O_3$  were detected as white deposit. In this study, the white deposit could be  $B_2O_3$  or the mixture of  $B_2O_3$  and  $WO_3$ . The experiments verify that the evaporation of  $WO_3$  could be depressed by the molten NaCl/KCl to a certain extent.

#### 4. Conclusions

$W_2B_5$  powder was successfully synthesized by the reaction between  $WO_3$  and amorphous B in NaCl/KCl flux at 1100 °C with the protection of flowing argon gas. The influences of calcining temperature and flux amount on the phases of the synthesized material were investigated. The presence of NaCl/KCl flux remarkably lowers the reaction temperature of the borothermal reduction because the mass transfer of the reactants was much faster in flux than in solid. However, too much flux was also unfavourable for the proceeding of the reaction. In this study, when the weight of NaCl/KCl was 10 times that of  $WO_3/B$ , pure phase  $W_2B_5$  powder could be synthesized at 1100 °C for 1 h. The synthesized powder was composed of agglomerated nanoparticles. The oxidation of  $W_2B_5$  powder begins at 294 °C with the maximum rate at 454 °C.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Table 1**  
Summary of the synthesis of tungsten borides.

Synthesis method	Raw materials	Synthesis conditions	Products	Ref.
Gas-solid reaction	WCl <sub>2</sub> , B	800 °C/0.5 h/Ar/excessive B	WB <sub>2</sub> layer on boron substrate	[9]
Solid-state reaction	W, B	1400 °C/1 h/vacuum/excessive B	WB <sub>2</sub> powder	[10]
Solid-state reaction	W, B	Arc-melted/Ar/excessive B	WB <sub>4</sub> bulk	[11,12]
Solid-state reaction	W, B	1500 °C/5 h/Ar/excessive B	W <sub>2</sub> B, WB, W <sub>2</sub> B <sub>5</sub> and WB <sub>4</sub> powders	[13]
Elements reaction in metal solutions	W, B, Al or Cu	1500 °C/5 h/Ar/excessive B	WB, δ-WB and WB <sub>2</sub> crystals	[14]
Molten salt method	W, B, NaCl/KCl	1000 °C/3 h/Ar	WB <sub>2</sub> powder	[15]
Combustion synthesis involving borothermal reduction	WO <sub>3</sub> , B, W	Ar/excessive B	W <sub>2</sub> B <sub>5</sub> powder with WB	[16]
Self-propagating high-temperature synthesis	CaWO <sub>4</sub> , B <sub>2</sub> O <sub>3</sub> , Mg	Ar/excessive B <sub>2</sub> O <sub>3</sub>	W <sub>2</sub> B <sub>5</sub> powder with WB	[17]
Double self-propagating high-temperature synthesis	CaWO <sub>4</sub> , B <sub>2</sub> O <sub>3</sub> , Mg	Ar/excessive B <sub>2</sub> O <sub>3</sub>	W <sub>2</sub> B <sub>5</sub> powder with WB and WB <sub>4</sub>	[18]
Mechanochemical synthesis	WO <sub>2.72</sub> , B <sub>2</sub> O <sub>3</sub> , Mg	30 h/Ar/excessive B <sub>2</sub> O <sub>3</sub>	W <sub>2</sub> B <sub>5</sub> powder	[19]
Double self-propagating high-temperature synthesis	WO <sub>3</sub> , B <sub>2</sub> O <sub>3</sub> , Mg	Ar/excessive B <sub>2</sub> O <sub>3</sub>	W <sub>2</sub> B <sub>5</sub> powder with WB and WB <sub>4</sub>	[20]
Borothermal reduction	WO <sub>2</sub> , B	1600 °C/1 h/vacuum	W <sub>2</sub> B <sub>5</sub> powder	[21]
Borothermal reduction in flux	WO <sub>3</sub> , B, NaCl/KCl	1100 °C/1 h/Ar	W <sub>2</sub> B <sub>5</sub> powder	This work

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