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Preparation of tungsten borides by combustion synthesis involving borothermic reduction of WO_3

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Abstract

An experimental study on the preparation of two tungsten borides, WB and W_2B_5, was conducted by self-propagating high-temperature synthesis (SHS), during which borothermic reduction of WO_3 and elemental interaction of W with boron proceeded concurrently. Powder mixtures with two series of molar proportions of WO_3:B:W = 1:5.5:x (with x = 1.16–2.5) and 1:7.5:y (with y = 0.5–1.33) were adopted to fabricate WB and W_2B_5, respectively. The starting stoichiometry of the reactant compact substantially affected the combustion behavior and the phase composition of the final product. The increase of metallic tungsten and boron reduced the overall reaction exothermicity, leading to a decrease in both combustion temperature and reaction front velocity. The initial composition of the reactant compact was optimized for the synthesis of WB and W_2B_5. In addition to small amounts of W_2B and W_2B_5, the powder compact of WO_3 + 5.5B + 2 W produced WB dominantly. Optimum formation of W_2B_5 was observed in the sample of WO_3 + 7.5B + 0.85W. Experimental evidence indicates that an excess amount of boron about 10–13% is favorable for the formation of WB and W_2B_5.

Keywords: Tungsten borides; WO_3; Self-propagating high-temperature synthesis (SHS); X-ray diffraction

1. Introduction

Considerable interest in the transition metal borides is mainly attributed to their unique combination of many promising properties, such as high melting points, high hardness, good electrical and thermal conductivity, chemical inertness, and excellent wear and corrosion resistance [1,2]. Formation of a variety of transition metal borides, including the Ti–B, Zr–B, Hf–B, V–B, Nb–B, and Ta–B compounds, has been conducted by combustion synthesis of constituent elements in the mode of self-propagating high-temperature synthesis (SHS) [3–9]. The SHS process takes advantage of the self-sustaining merit from highly exothermic reactions and hence has the potential of time and energy savings [10–13]. However, when direct combustion between the metal and boron is not feasible, the SHS process involving borothermic reduction of metal oxides has been considered as an alternative of preparing the related metal borides [14]. For example, molybdenum borides (Mo_2B, MoB_2, and Mo_2B_5) were produced from solid state combustion of the powder compacts composed of MoO_3, Mo, and boron [15]. Chromium borides (Cr_5B_3, CrB, and CrB_2) in either monolithic or composite form were fabricated through the SHS process involving reduction of Cr_2O_3 by boron [16].

Of particular interest for this study are tungsten borides which are well-known abrasive, corrosion-resistant, and electrode materials. There are four boride phases, W_2B, WB, W_2B_5 (or referred as WB_2), and WB_4, in the W–B binary system [17]. The boride W_2B_5 has been a promising reinforcement for carbon materials and refractory carbides such as B_4C and WC [18–20]. The addition of WB to MgB_2 enhanced the superconducting properties [21]. With field-activated combustion synthesis [22–24], WB_2 was shown to form solid solutions with TiB_2 and CrB_2 from elemental reactants. Itoh et al. [25] prepared various tungsten borides by solid state reactions between tungsten and boron powers at 800–1550 °C, and indicated that optimum production of WB and W_2B_5 was attained in the samples with a nearly 10 at.% excess of boron. Peshev et al. [26,27] performed a series of experiments on the borothermic reduction of different metal

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oxides between 1000 and 1750 °C to prepare the corresponding metal borides, including CrB_2, Mo_2B_5, W_2B_5, VB_2, NbB_2, and TaB_2.

Because heats of formation of tungsten borides around 66–118 kJ/mole are much smaller than those of TiB_2 (315.9 kJ/mol), ZrB_2 (322.6 kJ/mol), VB_2 (203.6 kJ/mol), and TaB_2 (209.2 kJ/mol) [28,29], self-sustaining combustion synthesis cannot be achieved in a powder compact composed of elemental tungsten and boron due to the weak exothermicity. As the first attempt, this study takes advantage of the highly energetic nature of reduction of the transition metal oxide and aims to investigate the preparation of tungsten borides, WB and W_2B_5, by means of the SHS route involving borothermic reduction of WO_3. The influence of sample stoichiometry was explored on the phase composition of the final product, sustainability of the combustion process, propagation velocity of the combustion front, and combustion temperature.

2. Experimental methods of approach

Tungsten oxide WO_3 (Strem Chemicals, 99.8% purity), elemental tungsten (Strem Chemicals, 12 μm, 99.9% purity) and amorphous boron (Noah Technologies Corp., 92% purity) were employed as the starting materials. Reactions (1) and (2) express formation of WB and W_2B_5, respectively, from WO_3, B, and W under exact stoichiometric proportions:

$$WO_3 + 5B + 2W \rightarrow 3WB + B_2O_3 \quad (1)$$

$$WO_3 + 7B + W \rightarrow W_2B_5 + B_2O_3 \quad (2)$$

According to previous studies on the preparation of metal borides [16,25,26], an excess amount of boron was suggested to account for the loss of boron through evaporation during the high-temperature synthesis process. Therefore, two initial reactant compositions modified from Reactions (1) and (2) are adopted in this study to consider additional boron and variable tungsten. The first series of samples is formulated by the composition of WO_3:B:W = 1:5.5:x and x = 1.16–2.5, signifying the content of metallic tungsten ranging 15.1–27.8 mol% in the powder mixture. The second composition possesses the reactant proportion as WO_3:B:W = 1:7.5:y and y = 0.5–1.33, corresponding to 5.56–13.5 mol% of tungsten.

The reactant powders with a prescribed composition were dry mixed in a ball mill and then cold-pressed into cylindrical test specimens with a diameter of 7 mm, a height of 12 mm, and a compaction density relative to 55% of the theoretical maximum density (TMD). The SHS experiment was conducted in a stainless-steel windowed chamber under an atmosphere of high-purity argon (99.99%). Details of the experimental setup and measurement approach were reported elsewhere [30].

3. Results and discussion

3.1. Observation of combustion characteristics

Fig. 1 illustrates a typical SHS sequence associated with self-propagating combustion of the WO_3–B–W powder compact. As revealed in Fig. 1, shortly after initiation the combustion front forms several localized reaction zones moving along a spiral trajectory on the sample surface. Even though self-sustaining combustion is achieved, the appearance of a spinning combustion wave instead of a planar reaction front implies that the heat flux generated from the solid state reaction is marginally sufficient. According to Ivleva and Merzhanov [31], once the heat flux liberated from self-sustaining combustion is no longer adequate to maintain the steady propagation of a planar front, the combustion front forms one or several localized reaction zones. Therefore, the spinning combustion wave is largely attributed to the weak reaction exothermicity of the reactant mixture. In general, the particle size and compaction density have an effect on the propagation rate of the combustion front due to the change in the contact surface area and heat transfer rate [32,33], while they cause no influence on the reaction exothermicity. With an aid of the external heat input such as sample preheating [7] and electric-field activation, a planar combustion front propagating longitudinally can be established for the SHS system of relatively low exothermicity.

In addition, the progression of the combustion wave is accompanied by plenty of misty products expelling from the

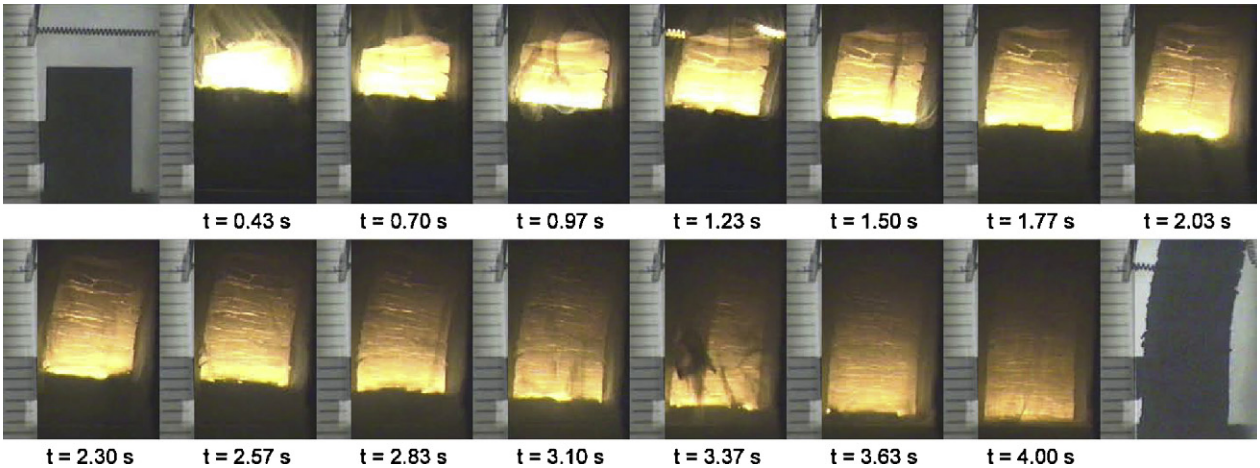

Fig. 1. Recorded images illustrating propagation of self-sustaining combustion along a powder compact with stoichiometry of $WO_3 + 5.5B + 2W$.

burned sample, resulting in significant delamination and elongation of the end product. According to previous studies [15,16], the ejected misty substance is believed to be B_2O_3 in the form of very fine liquid droplets. B_2O_3 is the by-product of the displacement reaction of WO_3 with boron. Such a loss causes the absence of B_2O_3 in the final products.

3.2. *Measurement of flame-front propagation velocity and combustion temperature*

The propagation velocity (V_f) of the reaction front in the axial direction was determined from the recorded SHS sequence with 30 images per second. The data with high accuracy were deduced. As shown in Fig. 2, the flame-front velocity varies in the range of 1.6–3.0 mm/s and decreases with increasing elemental tungsten for both series of the powder mixtures. The fluctuation of flame-front velocity is within 4%. Moreover, the samples with a less amount of boron (i.e., the composition of $WO_3 + 5.5B + xW$) generally had a higher combustion velocity. The composition dependence of the combustion velocity is most likely attributed to the variation of reaction exothermicity with initial stoichiometry of the reactant compact.

Four temperature profiles recorded from solid state combustion of the powder compacts of $WO_3 + 5.5B + xW$ with different tungsten amounts of $x = 1.16–2.33$ are depicted in Fig. 3, where the abrupt rise in temperature signifies rapid arrival of the combustion front and the peak value represents the reaction front temperature. As shown in Fig. 3, the combustion front temperature decreases from 1541 to 1347 °C with increasing metallic tungsten. This is caused by the fact that the borothermic reduction of WO_3 releases about 429 kJ of the reaction heat per unit mole of WO_3 [28], which is much more exothermic than the reaction between tungsten and boron. Namely, the reduction WO_3 by boron is the major energy contributor to self-sustaining combustion of the WO_3–B–W powder compact. Therefore, the additional boron and tungsten for the formation of tungsten borides reduced the overall reaction exothermicity, which is responsible for the decrease of both combustion temperature and reaction front velocity.

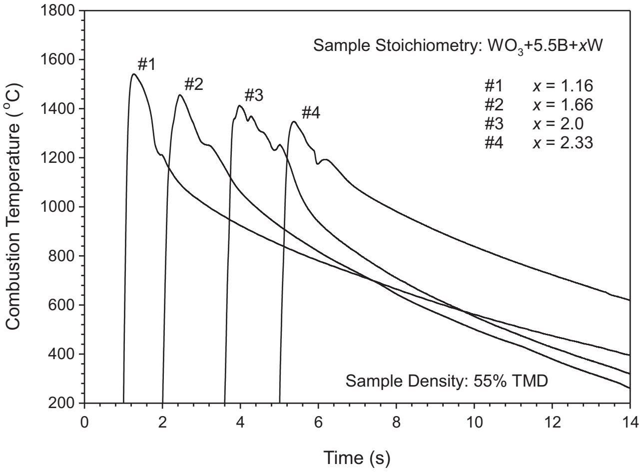

Fig. 3. Effect of elemental tungsten (W) content on combustion temperature of powder compacts with stoichiometry of $WO_3 + 5.5B + xW$.

Similarly, due to the dilution effect the combustion front temperature of the sample with stoichiometry of $WO_3 + 7.5B + yW$ decreases from 1433 to 1232 °C with increasing tungsten content from $y = 0.5$ to 1.33 (Fig. 4). When compared to that of the sample with $WO_3 + 5.5B + xW$, the lower reaction temperature for the powder compact of $WO_3 + 7.5B + yW$ is because of a higher proportion of elemental reactants included in the overall synthesis process. Most importantly, it should be noted that the variation of combustion temperature with sample stoichiometry is in a manner consistent with that of flame-front velocity.

3.3. *Phase constituents of combustion products*

The XRD patterns of the products synthesized from the powder compacts of $WO_3 + 5.5B + xW$ with $x = 1.16$, 2.0 and 2.33 are presented in Fig. 5(a)–(c), indicating formation of WB

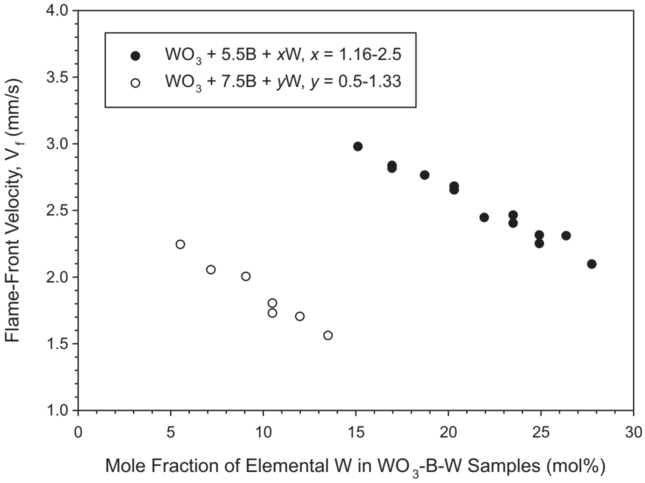

Fig. 2. Effect of elemental tungsten (W) content on flame-front propagation velocity of WO_3–B–W powder compacts.

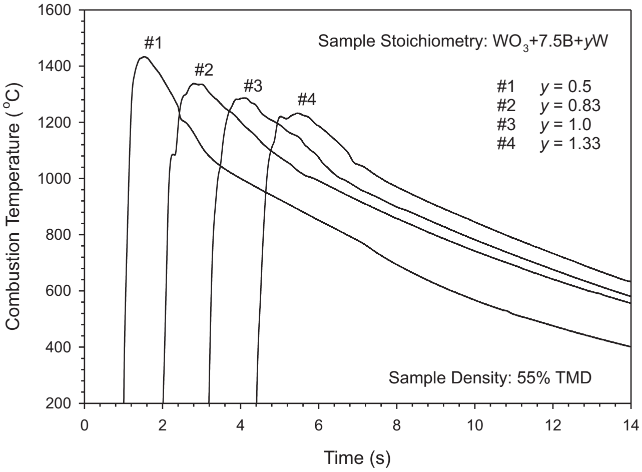

Fig. 4. Effect of elemental tungsten (W) content on combustion temperature of powder compacts with stoichiometry of $WO_3 + 7.5B + yW$.

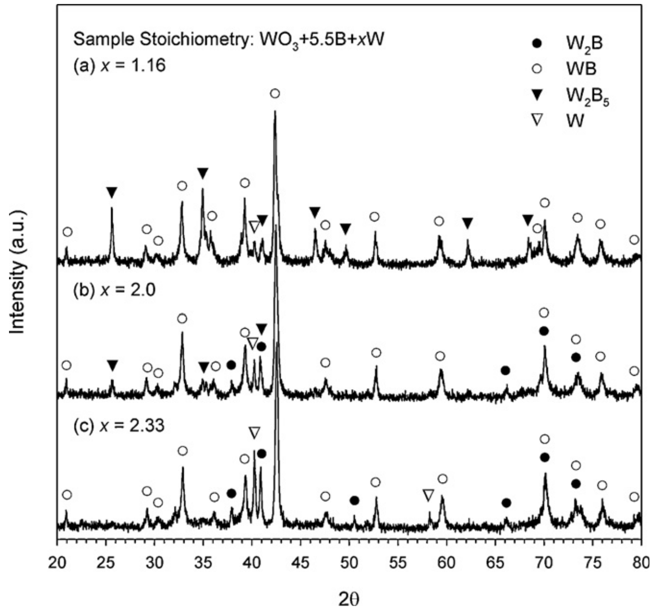

Fig. 5. XRD patterns of synthesized products from samples of WO_3 + 5.5B + xW with (a) $x = 1.16$, (b) $x = 2.0$, and (c) $x = 2.33$.

as the dominant boride phase from this series of samples. Moreover, Fig. 5 reveals that with the increase of metallic tungsten, the secondary boride is transformed from a B-rich phase W_2B_5 to a W-rich phase W_2B and more elemental tungsten is residually present. In general, for the powder compacts with $x < 2.0$, W_2B_5 was formed along with WB. When metallic tungsten increased up to $x > 2.0$, the resulting products contained WB as well as W_2B. Though both W_2B_5 and W_2B are detected in the product of the sample with $x = 2.0$, as depicted in Fig. 5(b), their contents are much less than that of the dominant phase WB. When compared to Reaction (1), the initial composition with an excess amount of boron around 10% (i.e., WO_3 + 5.5B + 2W) was shown to promote the formation of WB to the greatest extent.

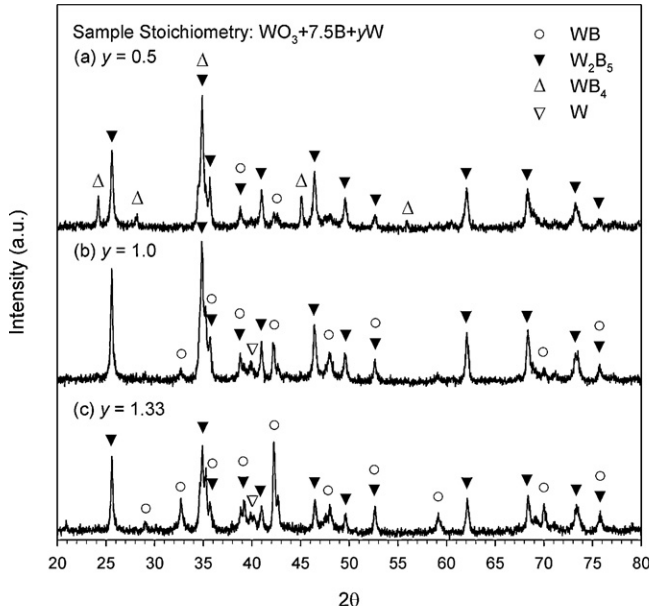

Fig. 6. XRD patterns of synthesized products from samples of WO_3 + 7.5B + yW with (a) $y = 0.5$, (b) $y = 1.0$, and (c) $y = 1.33$.

Fig. 6(a)–(c) shows the phase constituents of the final products obtained from samples of $WO_3 + 7.5B + y$W with $y = 0.5$, 1.0 and 1.33. The dominant boride formed from this series of samples is identified as W_2B_5. Fig. 6(a) reveals that for the sample with metallic tungsten at $y = 0.5$, there are two minor phases WB_4 and WB present in the final product. An increase in elemental tungsten converted the B-rich phase WB_4 into W_2B_5 and WB. Consequently, for the samples of $y \geq 0.85$, as shown in Fig. 6(b) and (c), the final products are composites of W_2B_5 and WB, and the amount of WB increases with initial tungsten content. In this study, optimum yield of W_2B_5 was obtained from the sample of $WO_3 + 7.5B + 0.85$W, which contains about 13% more boron than the stoichiometric amount. Similar to the case of WB, excessive boron is confirmed to facilitate the production of W_2B_5.

4. Conclusions

This study presents an experimental investigation on the preparation of tungsten borides, WB and W_2B_5, through combustion synthesis involving borothermic reduction of WO_3 and the elemental reaction of W with boron. In this study, the combustion wave of the WO_3–B–W powder compact propagated along the sample in a spinning mode. The starting stoichiometry of the sample was found to affect the combustion behavior and the phase composition of the final product.

Combustion synthesis of WB was performed by using the powder compacts of WO_3 + 5.5B + xW and x = 1.16–2.5. The increase of metallic tungsten led to a decrease in the overall reaction exothermicity, which was responsible for the decline of the combustion temperature from 1541 to 1302 °C and the descent of the reaction front velocity from 3.0 to 2.1 mm/s. Optimum formation of WB was observed in the sample of WO_3 + 5.5B + 2W. In addition to WB, the borides W_2B_5 and W_2B were identified as the secondary phases in the resulting products from this series of samples.

The powder compacts with initial stoichiometry of WO_3 + 7.5B + yW and y = 0.5–1.33 were adopted to prepare W_2B_5. Similarly, the combustion temperature decreased from 1433 to 1232 °C and reaction velocity from 2.2 to 1.6 mm/s with increasing metallic tungsten content. Most of the final products were composed of W_2B_5 as the major phase and WB as the minor phase. Among them, the synthesized product from the sample of WO_3 + 7.5B + 0.85W contains the least amount of WB.

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