Preparation of Cast Mo₂B₅ by Self-Propagating High-Temperature Synthesis Metallurgy Methods

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Received February 12, 2018; in final form, May 24, 2018

Abstract—This paper reports the preparation of cast dimolybdenum pentaboride by a self-propagating hightemperature synthesis (SHS) metallurgy method. Experiments were carried out in SHS reactors at an initial excess gas (Ar) pressure $p_0 = 5$ MPa. In the experiments, we used thermite-type starting mixtures consisting of molybdenum oxide, aluminum, boron oxide, and elemental boron powders. The combustion of such mixtures yields two types of final product: Mo₂B₅ and Al₂O₃. The combustion temperatures of the starting mixtures used in our experiments have been shown to exceed the melting points of the final products, which are thus formed in a liquid (cast) state. Under the effect of gravity, the heavier phase Mo₂B₅ settles down to form a lower ingot, whereas the lighter phase Al₂O₃ forms an upper ingot. The synthesis products have been characterized by X-ray diffraction and local microstructural analysis. The results demonstrate that the composition and amount of the starting mixture have a significant effect on the synthesis parameters and the composition and microstructure of the Mo₂B₅. We have optimized conditions for the preparation of single-phase cast dimolybdenum pentaboride.

Keywords: boride ceramics, cast dimolybdenum pentaboride, self-propagating high-temperature synthesis metallurgy, combustion, crystallization, phase composition, microstructure **DOI:** 10.1134/S0020168518120051

INTRODUCTION

Metal borides constitute an important and large class of inorganic compounds possessing low fusibility and high chemical stability in various aggressive media and exhibiting metal-like behavior, which shows up as high electrical and thermal conductivity, magnetic properties, and an unusual electronic structure. Their high hardness in combination with plastic properties and chemical inertness open up great possibilities for the use of borides as abrasive tools capable of ensuring high-quality surface finish and materials for cutting tools and tool steel heavily doped with borides. They are also used as alloys with some transition metals for the fabrication of critical parts; for boronizing articles made from steel and other metals in order to improve their hardness, wear resistance, and corrosion resistance; and as catalysts and semiconductors [1-4].

The Mo–B system is known to contain six boride phases: Mo₂B, Mo₃B₂, α - and β -MoB, MoB₂, and Mo₂B₅. According to its phase diagram (Fig. 1), the higher molybdenum boride is Mo₂B₅ (calculated boron content, 22 wt %). (Actually, there is boron deficiency: boron content of this boride does not exceed 19.5–20.8 wt %.) This phase is an imperfect structure with the ideal composition Mo₂B₅. At a temperature of 1600°C, it transforms into a phase with the MoB_2 structure, which melts at ~2100°C [5]. Dimolybdenum pentaboride has a wide homogeneity range: 66.7-70 at % boron. It is insoluble in water and has $t_{\rm m} = 1600^{\circ}$ C and $\rho = 7.2$ g/cm³ [6]. The best known process for the preparation of Mo₂B₅ is reaction between MoO₃, boron carbide, and carbon black. In a vacuum from 10^{-2} to 10^{-1} mm Hg at temperatures from 1200 to 1300°C, this reaction reaches completion in 0.5°C 1 h. Dimolybdenum pentaboride can also be prepared by heating a mixture of molybdenum and boron powders in a hydrogen atmosphere at a temperature from 1500 to $1600^{\circ}C (2Mo + 5B = Mo_2B_5)$. Yet another process for its synthesis is heating a mixture of molybdenum, boron oxide, and boron carbide in a hydrogen atmosphere at a temperature of 2000°C $(28Mo + 5B_2O_3 + 15B_4C = 14Mo_2B_5 + 15CO)$. It is worth noting that all of the existing industrial dimolybdenum pentaboride preparation processes require much energy and have low efficiency.



Fig. 1. Phase diagram of the Mo–B system.

In this respect, self-propagating high-temperature synthesis (SHS) appears very attractive [7-10]. One promising direction in this approach is SHS metallurgy. This method utilizes mixtures of metal oxides, a metallic reducing agent (aluminum), and a nonmetal (carbon, boron, or silicon). Combustion temperatures of such mixtures typically exceed the melting points of the starting reagents and the final products, which are formed in a liquid (cast) state in a combustion wave. This approach was used to obtain a large number of cast borides, silicides, and carbides of refractory metals and related composite materials [11-13].

The purpose of this work is to study fundamental aspects of the preparation of cast Mo_2B_5 by the SHS metallurgy method.

EXPERIMENTAL

In our experiments, we used mixtures of analyticalgrade molybdenum(VI) oxide and pure-grade boron(III) oxide with ASD-1 aluminum and boron. Starting mixtures were burned in guartz and graphite beakers 20 and 80 mm in diameter and 50 and 100 mm in height, respectively. The weight of the mixtures was 20 or 2000 g. It is worth noting that the synthesis under atmospheric conditions was accompanied by severe scatter of products from the reaction vessel because of the formation of a large amount of final and intermediate gaseous combustion products and the high MoO₃ volatility, which can be suppressed by creating an excess gas (Ar) pressure in the reactor. In view of this, all of the experiments were carried out in 3- and 20-L SHS reactors at an initial gas pressure $p_0 =$ 5 MPa. We used both stoichiometric mixtures and mixtures containing an excess of the boron-containing component and deficient in aluminum relative to the stoichiometric composition. The ratio of the reagents was calculated for the following chemical reactions:

1. $4MoO_3 + 18Al + 5B_2O_3 \rightarrow 2Mo_2B_5 + 9Al_2O_3(X)$, 2. $2MoO_3 + 4Al + 5B \rightarrow Mo_2B_5 + 2Al_2O_3(Y)$, 3. X/Y = 0.5/0.5, 4. $0.9(X/Y) + 0.1(Al/B_2O_3)$.

In our experiments, we visually observed the synthesis process through the inspection holes of the SHS reactor. The initial and final (maximum) pressures in the reactor were monitored with a standard pressure gage. Separation into the desired boride phase and an oxide phase was quantified by the yield of the desired product to the ingot (η_v) , which was calculated as $\eta_v =$ $(M_{\rm MB}/M_{\rm mix}) \times 100\%$, where $M_{\rm MB}$ is the mass of the ingot of the desired product and M_{mix} is the mass of the starting mixture. The scattering process (ejection of material from the reaction vessel) was quantified by the degree of scatter (η_s), which was calculated as $\eta_s =$ $\Delta m/M_{\rm mix}$) × 100%, where $\Delta m = M_{\rm i} - M_{\rm f}$ is the mass of the material ejected from the reaction vessel, $M_{\rm f}$ is the final mass of the vessel with the synthesis products, and $M_{\rm i}$ is the initial mass of the vessel with the starting mixture.

The phase composition of the desired products was determined by X-ray diffraction on a DRON-3M diffractometer with Cu K_{α} radiation. The phases present were identified using Powder Diffraction File (PDF) data. For microstructural characterization and elemental analysis of the structural components of the desires products, we used a Zeiss Ultra Plus ultrahigh-



Fig. 2. Appearance of the synthesis products. The upper and lower ingots consist of Al_2O_3 and Mo_2B_5 , respectively.

resolution field emission scanning electron microscope (based on the Ultra 55).

EXPERIMENTAL RESULTS

Visual observations and video recording of the combustion process, as well as X-ray diffraction characterization and local microstructural analysis of the synthesis products, provided a qualitative idea of the synthesis process. The combustion temperature of mixtures 1–4 exceeded the melting point of the synthesis products, which were thus obtained in a liquid state. In general, the synthesis process consists of three sequential steps. The first step is combustion and chemical transformation of the components of the starting mixtures (MoO₃, B₂O₃, B, and Al) into a twophase melt (high-temperature synthesis). The second step is the gravity separation of the combustion products ($Mo_x B_y$ boride and Al_2O_3 oxide phases), which produces two layers: upper, consisting of the "light" oxide (Al_2O_3) , and lower, consisting of the "heavy" $Mo_x B_y$ boride. The third step is cooling and the forma-



Fig. 3. X-ray diffraction pattern of the molybdenum boride prepared from mixture 1 ($M_{\text{mix}} = 20$ g, stoichiometric composition: $\Delta_{\text{B},\text{O}_3/\text{Al}} = 0\%$).

tion of the phase composition and crystal structure of the metallic and oxide layers.

After cooling and crystallization, there was no bonding between the ingots, which were easy to separate mechanically (Fig. 2). The present experimental data are summarized in Table 1. It is seen that, during combustion of the stoichiometric mixture 1, the final pressure in the reactor is $p_f = 7$ MPa, the degree of scatter is $\eta_s = 5\%$, and the yield of the desired product (molybdenum boride) is $\eta_y = 32\%$.

According to the X-ray diffraction data, the major phase in the sample was Mo_2B_5 . We also observed lines of the AlBMo phase and Al_2O_3 . The presence of AlB_{10} also cannot be ruled out: its strongest lines were seen, whereas its other lines could not be separated from the

Mixture	System	<i>p</i> _f , MPa	$\eta_{\rm y} = (M_{\rm MB}/M_{\rm mix}) \times 100\%$	$\eta_{\rm s} = (\Delta m/M_{\rm mix}) \times 100\%$
1	$X = 4 MoO_3 / 18 Al / 5 B_2 O_3$	7	32	5
2	$Y = 2\text{MoO}_3/4\text{Al}/5\text{B}$	18	17	18
3	X/Y = 0.5/0.5 = 5MoO ₃ /11Al/2.5B ₂ O ₃ /2.5B	10	28	10
4	$0.9 (X/Y) + 0.1 (2Al/B_2O_3)$	9	29	8

Table 1. Synthesis parameters at different starting mixture compositions ($p_0 = 5$ MPa, $M_{mix} = 20$ g, $V_{reactor} = 3$ L)



Point	В	0	Al	Mo	Phase* composition
1		53.0	46.8	0.2	Al ₂ O ₃
2		52.4	47.5	0.1	Al_2O_3
3	22.8	0.7	0.4	76.1	Mo ₂ B ₅
4	22.1	0.3	0.2	77.4	Mo ₂ B ₅
5	8.4	0.2	18.9	72.5	MoAlB
6	8.2	0.4	19.8	71.6	MoAlB
7	80.2	0.5	19.1	0.2	AlB_{10}
8	81.1	0.3	18.2	0.4	AlB ₁₀

* Calculated from the elemental analysis and X-ray diffraction data.

Fig. 4. Microstructure and elemental composition (wt %) of the molybdenum boride prepared from mixture 1 ($M_{mix} = 20$ g, stoichiometric composition: $\Delta_{B_2O_3/A1} = 0\%$).

general background in the X-ray diffraction pattern (Fig. 3).

Figure 4 illustrates the microstructure and the elemental and phase compositions of the ingot. These data correlate well with the above X-ray diffraction results. The major phase is Mo_2B_5 (points 3 and 4). There are also the Al_2O_3 phase (points 1 and 2), the MoAlB eutectic (points 5 and 6), and a small amount of AlB_{10} (points 7 and 8). In the case of the combustion



Fig. 5. X-ray diffraction pattern of the molybdenum boride prepared from mixture 3 ($M_{\text{mix}} = 20$ g, stoichiometric composition: $\Delta_{B_2O_3/A1} = 0\%$).

INORGANIC MATERIALS Vol. 54 No 12 2018 of the stoichiometric mixture 2, we had $p_f = 18$ MPa, $\eta_v = 17\%$, and $\eta_s = 18\%$. It is worth noting that, in this case, the final pressure in the reactor and the degree of scatter were maximal, whereas the yield of the desired product was minimal. This suggests that the mixture in question is technologically unsuitable, because the combustion of large masses in a reactor may lead to a hazardous situation (because of the high final pressure), with a very low yield of the desired product. For this reason, this mixture was not used in subsequent experiments. In the case of the combustion of mixtures 3 and 4, the processes were similar in synthesis parameters and had low final (maximal) pressure, a low degree of scatter, and a high yield of the desired product. Thus, these compositions are the most attractive for the preparation of cast dimolybdenum pentaboride.

Figures 5 and 6 present the phase composition, microstructure, and elemental composition of the ingot prepared from the stoichiometric mixture 3 $(M_{\rm mix} = 20 \text{ g})$ in the 3-L SHS reactor. It is seen that, in addition to the major phase Mo_2B_5 , there is an appreciable amount of AlBMo. In the case of the combustion of 20 g of mixture 4, containing an excess of boron-containing reagents ($\Delta_{B_2O_3/Al} = 10\%$), no AlBMo was detected in the reaction products, which consisted largely of the molybdenum boride Mo₂B₅ and aluminum boride AlB_{10} (Figs. 7, 8). The X-ray diffraction pattern in Fig. 7 contains reflections from not only Mo₂B₅ but



Point	В	Al	Мо	Phase*. composition
1	21.01	0.3	78.6	Mo ₂ B ₅
2	21.6	0.4	78.0	Mo ₂ B ₅
3	8.5	19.7	71.8	MoAlB
4	8.2	19.9	71.9	MoAlB
5	21.2	0.2	78.6	Mo ₂ B ₅
6	21.9	0.6	77.5	Mo ₂ B ₅

* Calculated from the elemental analysis and X-ray diffraction data.

Fig. 6. Microstructure and elemental composition (wt %) of the molybdenum boride prepared from mixture 3 ($M_{\text{mix}} = 20$ g, stoichiometric composition: $\Delta_{B_2O_3/A1} = 0\%$).

also AlB_{10} . It is worth noting that, despite the appreciable intensity of the reflections from AlB_{10} , the percentage of this phase is relatively small: it has a higher reflecting power than does Mo_2B_5 . This follows as well from analysis of the data presented in Fig. 8.

As shown earlier [14, 15], increasing the mass of the starting mixture (scale factor) leads to an increase in the percentage of the desired phase in the final product. For this purpose, we synthesized mixture 4, with an excess of boron-containing reagents ($\Delta_{B,O_3/Al} = 10\%$, $M_{mix} = 2$ kg).



Fig. 7. X-ray diffraction pattern of the molybdenum boride prepared from mixture 4 ($M_{mix} = 20$ g, excess $\Delta_{B_2O_3/Al} = 10\%$).

The X-ray diffraction pattern in Fig. 9 demonstrates that the major phase in the synthesis product is Mo_2B_5 . In addition, there are weak lines (at the level of the background) characteristic of AlB_{10} and AlBMo. Figure 10 illustrates the microstructure and elemental and phase compositions of the synthesis product obtained in the last experiment. It is seen that the desired product consists almost entirely of dimolybdenum pentaboride. Small amounts (under 3%) of AlB_{10} and AlBMo can be present as intergranular phases.

DISCUSSION

Analysis of the combustion process and final products shows that, in the case of the combustion of mixture 1, the reaction product contains a large amount of oxide inclusions. This is due to the low combustion temperature, as a result of which the "lifetime" of the melt is short, so that the Al_2O_3 and Mo_2B_5 phases cannot fully separate. This is also evidenced by the low final (maximum) pressure in the reactor ($p_f = 7 \text{ MPa}$) and the low degree of scatter ($\eta_s = 5\%$). Mixture 2 seems to have a very high combustion temperature, which leads to the formation of a large amount of gaseous products. As a result, the final pressure in the reactor reaches a very high level ($p_f = 18$ MPa), as does the degree of scatter of the material from the reaction vessel ($\eta_s = 18\%$). In this case, the final pressure in the reactor and the degree of scatter have maximum values, and the yield of the desired product has the min-

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Point	В	0	Al	Мо	Phase*. composition
1	22.7	0.5	0.3	76.5	Mo ₂ B ₅
2	22.5	0.2	0.1	77.2	Mo ₂ B ₅
3	80.4	0.4	19.0	0.2	AlB ₁₀
4	80.6	0.3	18.7	0.4	AlB ₁₀

* Calculated from the elemental analysis and X-ray diffraction data.

Fig. 8. Microstructure and elemental composition (wt %) of the molybdenum boride prepared from mixture 4 ($M_{\text{mix}} = 20$ g, excess $\Delta_{B,O_3/Al} = 10\%$).

imum value among all of the experiments carried out (Table 1). Mixture 3 is a 1 : 1 combination of the stoichiometric mixtures 1 and 2. In the case of the combustion of 20 g of this mixture, the reaction product consists of Mo_2B_5 , AlB_{10} , and eutectic MoAlB. Increasing the percentage of boron in the starting mixture causes eutectic MoAlB to disappear in the composition of the desired product. Combustion of a large mass of a mixture ($M_{mix} = 2 \text{ kg}$) in the reactor increases the "lifetime" of the melt, thereby leading to an increase in the extent of the reaction. As a result, the



Fig. 9. X-ray diffraction pattern of the molybdenum boride prepared from mixture 4 ($M_{mix} = 2 \text{ kg}$, excess $\Delta_{B_2O_3/Al} = 10\%$).

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desired product consists almost entirely of dimolybdenum pentaboride.

It is seen from the X-ray diffraction and local microstructural analysis results that all of the syntheses yielded the same phases, but their relative amounts differed significantly. As the synthesis conditions are varied, the synthesis product approaches the desired phase (Mo_2B_5), which prevails in the last sample (Figs. 9, 10). It is worth noting that, in most cases, the reflections from the Mo_2B_5 phase in X-ray diffraction patterns are rather narrow, which points to a well-formed crystal structure.

CONCLUSIONS

We have found conditions for the preparation of cast dimolybdenum pentaboride, Mo₂B₅, by the SHS metallurgy method. The microstructure and phase composition of reaction products obtained under various synthesis conditions have been determined by X-ray diffraction and local microstructural analysis. Taking into account results of previous research on the preparation of cast materials by SHS metallurgy methods, we have shown that the key parameters influencing the fundamental aspects of synthesis and the phase composition and microstructure of the final products are the initial pressure in the reactor and the composition and amount of the starting mixture. Varying these parameters, one can effectively control the fundamental aspects of the synthesis of cast dimolybdenum pentaboride. We have optimized conditions for the preparation of a single-phase product.



Point	В	Al	Мо	Phase composition*
1	21.0	0.4	78.6	Mo ₂ B ₅
2	22.1	0.1	77.8	Mo ₂ B ₅
3	20.8	0.1	79.1	Mo ₂ B ₅

* Calculated from the elemental analysis and X-ray diffraction data

Fig. 10. Microstructure and elemental composition (wt %) of the molybdenum boride prepared from mixture 4 ($M_{\text{mix}} = 2 \text{ kg}$, excess $\Delta_{B_2O_3/A1} = 10\%$).

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Translated by O. Tsarev