Preparation of single phase molybdenum boride

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ABSTRACT

The formation of MoB through volume combustion synthesis (VCS), and through mechanochemical synthesis (MCS) followed by annealing has been investigated. MoO_3, B_2O_3 and Mg were used as reactants while MgO and NaCl were introduced as diluents. Products were leached in dilute HCl solution and were subjected to X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) examinations. Mo was the major phase component in the VCS products under all the experimental conditions. Mo_2B, MoB, MoB_2 and Mo_2B_5 were found as minor phases. Products of MCS contained a mixture of Mo_2B, MoB, MoB_2 and Mo. After annealing the MCS product at 1400 °C for 3 h, single phase α-MoB was obtained.

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1. Introduction

A vast amount of research has been devoted to transition metal borides due to their high hardness, high-temperature strength, corrosion resistance, high melting points, chemical stability, wear resistance and electrical properties [1–5]. Most of the studies have been focused on preparation of TiB_2 or TiB_2 containing composites [6–12]. Molybdenum borides have been used as hard coating materials for high temperature structural applications, and also in the form of MoB/CoCr cermet coatings [1,2,13]. Additionally, MoB–$MoSi_2$ or Mo_2B_5–$MoSi_2$ compositions have been used as oxidation resistant composites [14] or coatings [2,15]. The Mo–B phase diagram (Fig. 1) contains 5 phases: Mo_2B, MoB, MoB_2, Mo_2B_5 and $Mo_{1-x}B_3$ (MoB_4) [16]. MoB exists in two allotropic forms: α-MoB is the low temperature phase having orthorhombic crystal structure and a solubility range of about 48.5–50.5 at% B; β-MoB is stable above 1800 °C, with tetragonal crystal structure.

For synthesis of molybdenum borides different methods have been explored such as mechanochemical [17] electrochemical [15,18], hydrothermal [1], self-propagating high-temperature syntheses (SHS) [2,19] and in situ displacement reactions [14]. Volume combustion synthesis (VCS) (also known as thermal explosion) is a synthetic method similar to the SHS. Both methods exploit the highly exothermic nature of the reactions to generate

a self-propagating process but possess different ignition methods. In the SHS, ignition is typically achieved by heating the upper surface of the reactants' pellet [2,3,5]. Once initiated the reaction propagates through the pellet "leaving behind" the products. Formation of various transition metal borides by SHS has been investigated in recent studies [2,3,5–7,19–21]. In the VCS, on the other hand, the reactants are heated altogether and reaction takes place at once. VCS exhibits most of the advantages of SHS, such as low cost, simplicity of the experimental set up and short reaction duration.

Mechanochemistry is another rather popular method for the synthesis of pure borides such as vanadium boride [4], titanium boride [6,22], molybdenum boride [17], and other borides [23,24], as well of composites containing borides [24–26]. Various nanocrystalline and non-equilibrium phases have been obtained by mechanochemistry [4,23–26]. In this method the reactants are subjected to high energy ball milling, during which severe plastic deformation, particle size reduction, intimate mixing, and mechanical activation are achieved [4,23–26]. Moreover, during milling process, the particles are cold welded to one another and then fractured repeatedly. This enhances diffusion. A reaction may take place during the milling process milling (gradually or all at once), or during a subsequent annealing step [24]. Products obtained from mechanochemical synthesis (MCS) were suggested to be free of side products, and to have a higher yield after leaching, as compared to VCS [6].

Despite the large number of synthetic methods applicable to the production of borides, there are only a few of studies concerning the preparation of molybdenum borides. In addition, in almost none of these studies, formation of single phase borides could be

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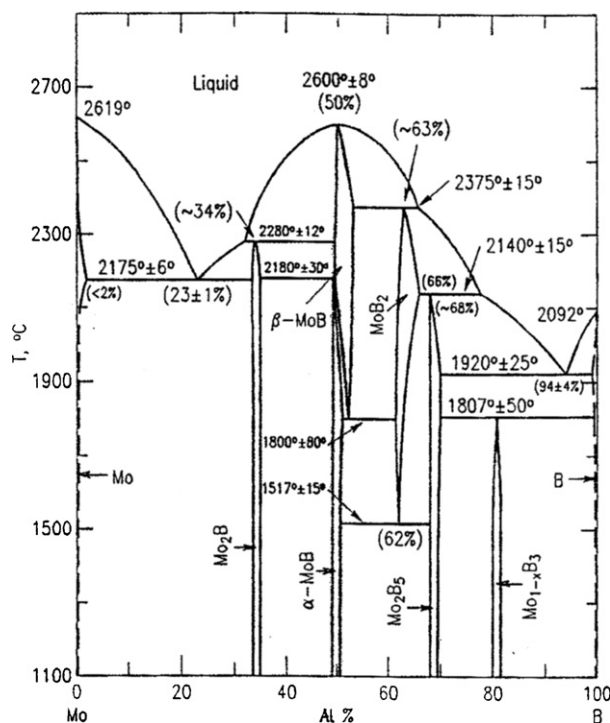*E-mail address:* erdemcamurlu@gmail.com

Fig. 1. Mo–B phase diagram [16].

demonstrated. Typically, a mixture of boride phases was formed (Table 1) [1,2,17–19,25,26]. In this perspective, no interpretations are available in the literature. Thus, the reasons for the formation of a boride mixture or for the formation of a given boride from a reactant mixture containing Mo and B in a different stoichiometric ratio remain unclear.

In literature, most of the studies describe the preparation of molybdenum borides starting from elemental Mo and B powders. On the other hand, in this study the formation of MoB was investigated using Mg, and cheap and readily available oxide materials, namely MoO_3 and B_2O_3. For this purpose, the volume combustion method as well as a combined method of mechanochemical synthesis and thermal treatment was examined.

2. Experimental procedures

MoO_3 (Merck, purity >99.5%) + B_2O_3 + Mg (Aldrich, −50 mesh, purity >99%) mixtures containing excess amounts of Mg and B_2O_3 were prepared according to the stoichiometry of Reaction (1). In this reaction MoO_3 and B_2O_3 are reduced by Mg and simultaneously; the so-formed Mo and B are then expected to react with each other to produce MoB. MgO (Merck, purity >98.0%) or NaCl (Merck, purity >99.5%) were added as diluents. B_2O_3 was produced by calcination of H_3BO_3 (Merck, purity >99.8%) at 900 °C for 2 h. The stoichiometric ratios of the starting mixtures are listed in Table 2. In a given experiment, the total amount of the reactants was 4 g (without diluents). Adiabatic temperatures of the reactions were calculated by Factsage software [27].

$$2MoO_3 + 9Mg + B_2O_3 + ((X)MgO\,or\,(Y)NaCl) = 2MoB + 9MgO \qquad (1)$$

Volume combustion synthesis experiments were conducted by inserting the reactant mixtures, placed inside graphite crucible, in a pot furnace preheated at 1000 °C. A schematic drawing of the VCS setup is given in Fig. 2. The graphite crucible had 7 cm inner and 8.5 cm outer diameters and a height of 14 cm. The lid of the graphite crucible was kept closed during the experiments. The lid contained two holes which were 8 mm in diameter. Through one hole a K type thermocouple sheathed with inconel was inserted and was kept in contact with the reactants throughout the experiments. Temperature of the reactants inside the crucible was measured by an on-line temperature measurement system and the data was recorded on a computer. Through the second hole an alumina tube was inserted for continuous supply of argon gas (at a rate of 3.33×10^{-5} m^3/s). After the reaction, the graphite crucible was removed from the furnace and was let cool down to room temperature under continuous argon flow. 1 g of VCS product was leached in 100 mL of 1 M HCl for 15 h [6].

MCS experiments were conducted in a planetary ball mill (Retsch PM100). Reactant mixtures in the stoichiometric ratio of sample C1 were placed in a stainless steel grinding jar (250 mL volume) with eight stainless steel balls (20 mm in diameter). Ball to powder weight ratio was kept at 15:1. The lid of the jar was closed air tight and 3 consecutive vacuum-argon cycles were applied through the valve on the lid. Ball milling was performed for durations ranging between 1 and 13 h. Products of MCS were leached in 1 M HCl for 30 min [6]. After leaching, the products were annealed at 1400 °C for 3 h under argon atmosphere in a tube furnace. Heating and cooling rates were 7 °C/min.

The free energies of reactions were calculated by Factsage software [27]. VCS and MCS products were subjected to powder X-ray diffraction (XRD) and scanning electron microscopy (SEM, JEOL JSM-6400) analyses. XRD analyses were carried out by a Rigaku Multiflex unit at a rate of 2°/min with Cu-Kα radiation.

3. Results and discussion

3.1. Volume combustion synthesis (VCS)

In VCS experiments, the reactions occurred 2–3 min after the graphite crucible was inserted in the pot furnace. The first experiment for VCS was performed by using $MoO_3 + Mg + B_2O_3$ mixture

Table 1
Summary of the previous studies on preparation of molybdenum borides by various methods.

Production method	Details	Reactants	Aimed products	Final products and phases	Strong and weak points
SHS [2,19]	Ignition (after preheating to 300 °C)	Mo, B or MoO_3, Mo, B [19] Mo, B, Si [2]	α-MoB Mo$_2$B MoB$_2$ Mo$_2$B$_5$ MoB$_4$ α-MoB, MoSi$_2$	α-MoB, Mo$_2$B Mo$_2$B, Mo, α-MoB MoB$_2$, α-MoB, β-MoB, Mo$_2$B$_5$ MoB$_2$, Mo$_2$B$_5$, α-MoB Mo$_2$B$_5$, MoB$_4$ α-MoB, β-MoB, MoSi$_2$, Mo$_5$Si$_3$	Only equimolar mixture of Mo and B was reported to be self sustaining. Preheating was required for higher borides [2]. In neither of the reactions the intended boride was obtained as single phase. Secondary borides, which contained dominantly MoB were also present.
MCS [17]	Ball milling then annealing at 1600 °C	Mo, B	MoB$_2$ Mo$_2$B$_5$	Mo, MoB$_2$ (after milling), MoB$_2$, Mo$_2$B$_5$ (after annealing) Mo$_2$B$_5$ (after annealing)	Single phase Mo$_2$B$_5$ was obtained.
MCS [25]	Ball milling then annealing at 1400 °C	Mo, B, Si	Mo/Mo$_5$SiB$_2$	Mo, Mo$_2$B, MoB, MoB$_2$, besides silicides	Direct synthesis of Mo and Mo$_5$SiB$_2$ composite powder could not be succeeded, most probably due to the formation of a mixture of borides in the system.
Hydrothermal [1]	In autoclave at 300 °C then annealing at 900 °C	MoO_3, KBH$_4$ and CCl$_4$	α-MoB	Mo, α-MoB	A mixture of boride phases and Mo formed after hydrothermal synthesis. After annealing at 900 °C, Mo and MoB formed. Although KBH$_4$ to MoO_3 ratio was 6, MoB having equimolar Mo and B formed.

Table 2
Molar ratios of reactants and diluents in the starting mixtures, phases present in VCS products as determined by XRD, measured ignition temperatures and calculated adiabatic temperatures [27].

| Sample designation	Molar ratio					Ignition Temperature (°C)	Phases present		
	MoO_3	Mg	B_2O_3	MgO (X) (diluent)	NaCl (Y) (diluent)		Major	Minor	Adiabatic temperature (°C) (Calculated[a])
C1	2	9.9	1.1	–	–	510	[b]	[b]	2398
C2	2	9.9	1.1	7	–	550	Mo	Mo_2B, MoB	2294
C3	2	9.9	1.1	14	–	590	Mo	Mo_2B, MoB	2120
C4	2	13.5	1.5	7	–	530	Mo	MoB, Mo_2B	2117
C5	2	13.5	1.5	–	12.5	320	Mo	MoB, MoB_2, Mo_2B_5	1337
C6	2	13.5	1.5	–	25	430	Mo	–	1086
C7	2	27	3	–	10	280	Mo	MoB_2	1130

[a] [27].
[b] Could not be determined.
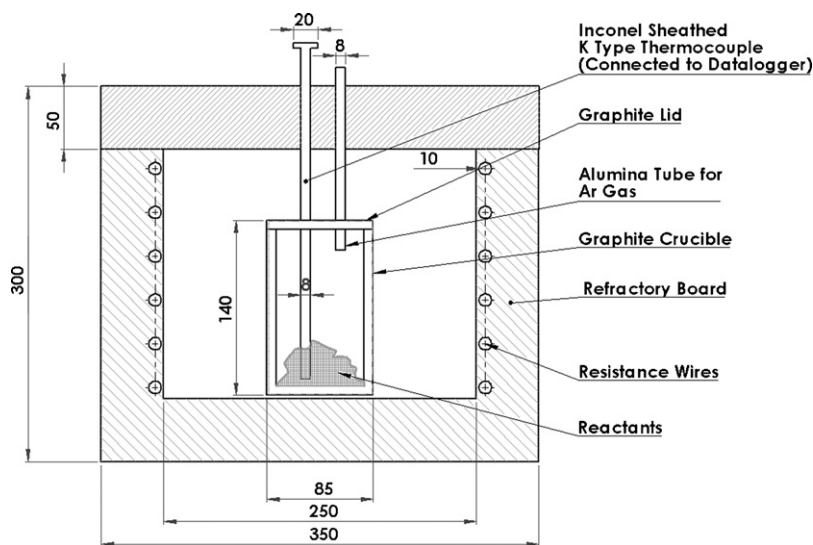
Fig. 2. Schematic drawing of VCS setup (dimensions are in mm).

without the addition of a diluent. Mg and B_2O_3 were used 10% in excess of the stoichiometry required for Reaction (1) as shown in Table 2 (Mixture C1 (Combustion 1)). A violent explosion took place when the temperature reached to about 510 °C, resulting in the loss of all the entire product form the reaction crucible. During the production of TiB_2 by VCS, an explosion did not occur [6]. The results of the first experiment show that the reaction is very violent and that precaution needs to be taken in order to preserve the products in the crucible.

In order to prevent the explosion, diluents (MgO and NaCl) were utilized. Adiabatic temperatures of Reaction (1) as a function of excess amounts of Mg and B_2O_3, and as a function of the amounts of MgO and NaCl are presented in the last column of Table 2 [27]. The amount of the diluent to be employed is a critical parameter. An insufficient amount can lead to an explosion, while an excess amount can prevent the ignition of the reaction. As reported in Table 2, NaCl was found to be more effective than MgO in reducing the adiabatic temperature. The characteristics of the diluents used in this study are listed in Table 3. It can be observed that the

calculated adiabatic temperatures of reactions are lower than the melting temperature of MgO and are higher than that of NaCl. The actual temperature attained during the reaction is expected to be lower than the calculated adiabatic temperature due to heat loss caused by the graphite crucible and by the thermocouple, which are in contact with the reactants. Consequently, NaCl may be in solid (or in liquid) state during the reactions and MgO is expected to remain in solid state.

When MgO or NaCl was introduced as diluents, at the amounts given in Table 2, the reactions took place with a non-explosive behavior and all of the products remained in the graphite crucible. A sudden release of smoke and an increase in the temperature indicated the occurrence of the reactions. The onset of temperature increase was recorded as the ignition temperature. The experiments conducted with MgO additions are labeled as C2, C3 and C4, and experiments conducted with NaCl additions are labeled as C5, C6 and C7 in Table 2. The ignition temperatures of the reactions are also listed. While the addition of MgO caused a slight increase in the ignition temperature, NaCl caused an unexpected decrease.

Table 3
Melting and boiling temperatures of reactants, products and diluents.

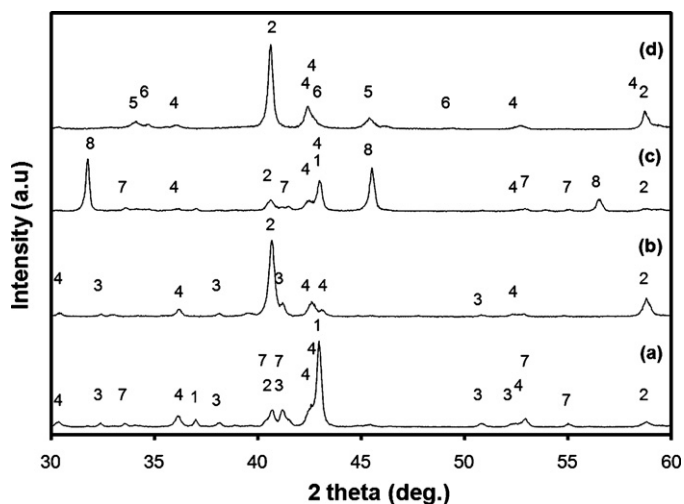|	Mg	B_2O_3	MoO_3	Mo	B	MoB	NaCl	MgO
Melting T (°C)	650[a]	450[a]	801[a]	2623	2075	2600[b]	801	2825
Boiling T (°C)	1094[a]	1860					1465	

[a] [27,28].
[b] [16].

Fig. 3. XRD patterns of the products obtained from volume combustion reactions of mixtures (a) C4, (b) C4 after leach, (c) C5, (d) C5 after leach (1: MgO, 2: Mo, 3: Mo_2B, 4: MoB, 5: MoB_2, 6: Mo_2B_5, 7: $Mg_3B_2O_6$, and 8: NaCl).

The role of NaCl in decreasing the ignition temperature is not clear and research for clarifying the effect of NaCl in this process is in progress.

The XRD patterns of products of C4 (MgO added) and C5 (NaCl added) mixtures are presented in Fig. 3a and c, respectively. It can be seen that the volume combustion products were composed of MgO, Mo, Mo_2B, MoB and $Mg_3B_2O_6$ (and NaCl). MgO is not only a product of Reaction (1) but also a diluent in the C4 mixture. After leaching the products in 1 M HCl for 15 h, MgO and $Mg_3B_2O_6$ (and NaCl) were removed (Fig. 3b and d). $Mg_3B_2O_6$ forms by the reaction of MgO and B_2O_3 and it is an undesired side product in the magnesiothermic production of borides due to the difficulty of removing it from the products by leaching [6,8,29]. It was previously found that 15 h was sufficient for removal of $Mg_3B_2O_6$ from VCS products by leaching in 1 M HCl [6]. Due to the facts that MgO is not inert towards B_2O_3 and that using MgO as the diluent causes an increase in the amount of $Mg_3B_2O_6$ in the products, NaCl was used instead of MgO. NaCl does not react with the product phases and does not form new or hard-to-leach phases, as opposed to MgO. The effect of NaCl has been investigated previously in other combustion synthesis systems [15,30,31]. When NaCl was used as the diluent, no crystalline compounds containing NaCl was detected in the products. As expected, the amount of $Mg_3B_2O_6$ was considerably reduced when NaCl diluent was used, as compared to the products of the experiments conducted with MgO diluent.

In all of the products Mo represented the major phase with minor amounts of Mo_2B, MoB_2, Mo_2B_5 as shown in Fig. 3b and d and in Table 2. The formation of a mixture of borides was reported previously in other studies aiming to the formation of single phase borides [1,25,26,29]. Mo forms in the system through the reduction of MoO_3 by Mg (Reaction (2)). Even when excess amounts of B_2O_3 and Mg were used in the reactant mixture, Mo remained in the products, and a complete formation of molybdenum borides was not achieved (Table 2). These results showed that production of molybdenum borides through combustion reactions is intricate even with the aid of diluents and excess stoichiometric amounts of Mg and B_2O_3.

$$MoO_3 + 3Mg = Mo + 3MgO \qquad (2)$$

Formation of TiB_2 [6,8] and ZrB_2 [32] by VCS from TiO_2 or ZrO_2, B_2O_3 and Mg mixtures was previously investigated and it was shown that through this method it is possible to achieve the formation of TiB_2 or ZrB_2 without elemental Ti or Zr or other boride
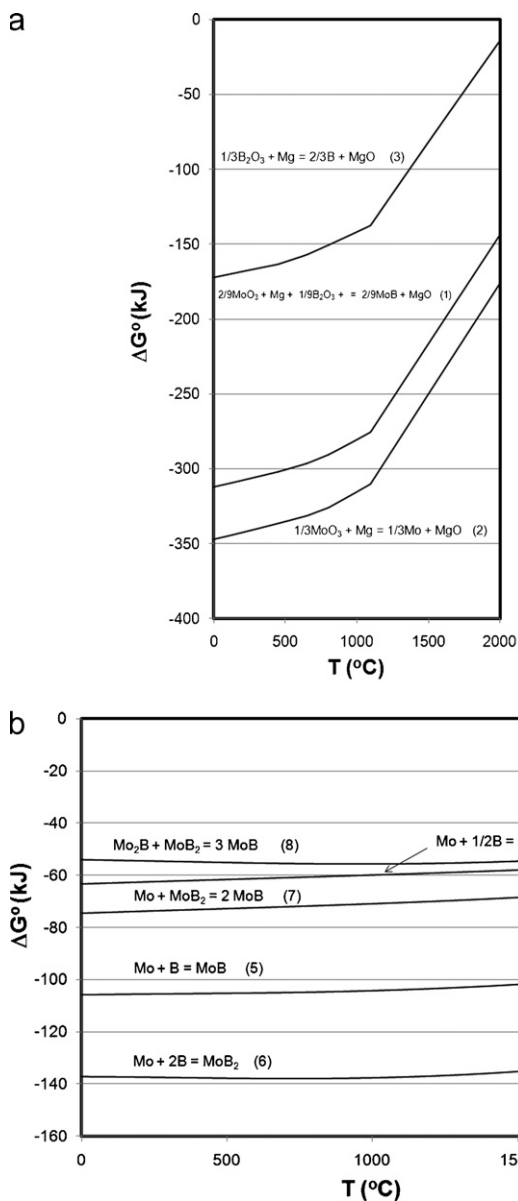

Fig. 4. Change in free energies of (a) Reactions (1)–(3) and (b) Reactions (4)–(8) with respect to temperature [27].

phases in the products. In these studies, complete conversion of TiO_2 or ZrO_2 into TiB_2 or ZrB_2 could be achieved [6,31]. The nature of the reaction appears to be different in the case of the formation of molybdenum borides by magnesiothermic reduction of MoO_3 and B_2O_3. This difference may be related to the high melting point of Mo, 2623 °C, which is higher than the adiabatic temperatures of the reactions given in Table 2, causing the permanence of Mo in the solid state during reactions. Moreover, it is important to note that the adiabatic temperatures presented in Table 2 were calculated for complete conversion of the reactants into products (Reaction (1)). The actual temperatures are expected to be lower than the calculated adiabatic temperatures for two reasons. One reason is the heat loss, caused by the graphite crucible and by the thermocouple, as mentioned. The other is the lack of completion of the reactions as shown by XRD analyses which reveal that metallic Mo is still present in the product. Since diffusion is much slower in solid state, it is not surprising that the reaction between Mo and B was incomplete. Similarly, unreacted W and a mixture of tungsten borides were observed in the products of SHS reaction of $CaWO_4$,
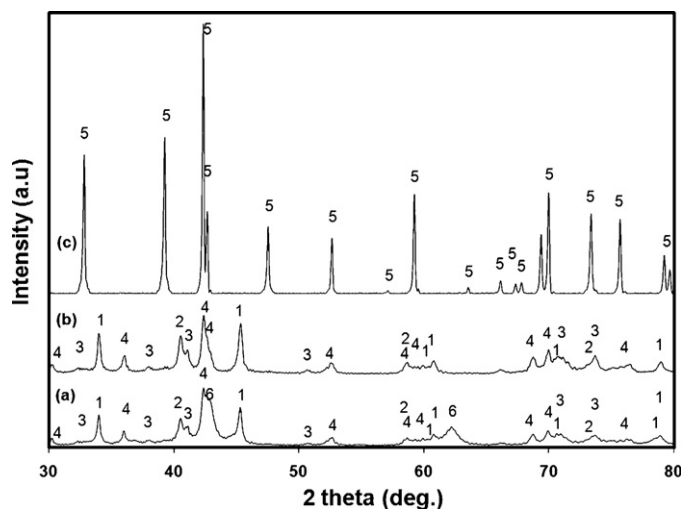
Fig. 5. XRD patterns of the products after (a) MCS, (b) leaching MCS product and (c) annealing the leach product at 1400 °C in argon atmosphere for 3 h. (1) MoB$_2$, (2) Mo, (3) Mo$_2$B, (4) β-MoB, (5) α-MoB, and (6) MgO.

B$_2$O$_3$ and Mg [29]. Also in this case the presence of unreacted elemental W and a mixture of tungsten borides during preparation of tungsten borides from oxides can be addressed to the high melting point of W [29].

Overall formation reaction of MoB (Reaction (1)) can be represented as (i) reduction of MoO$_3$ by Mg, (ii) reduction of B$_2$O$_3$ by Mg, and (iii) reaction of Mo and B to form molybdenum borides, as shown in Reactions (2), (3) and (4)–(6), respectively. The incomplete occurrence of Reaction (1) may be due to the lack of completion of one of these steps. Free energy of Reaction (2) is negative, as shown in Fig. 4a [27] and the absence of MoO$_3$ together with the presence of Mo in the reaction products indicate that Reaction (2) achieved completion. The presence of B$_2$O$_3$ or B cannot be determined by XRD analysis due to their amorphous structure. However, the negative free energy of Reaction (3) (Fig. 4a) and the fact that Reaction (3) was observed to occur completely with the formation of TiB$_2$ or ZrB$_2$ when the same method was employed [6,8,32], support the occurrence of Reaction (3) in the system.

$$B_2O_3 + 3Mg = 2B + 3MgO \qquad (3)$$

Free energies of formation of the borides by the reaction of elemental Mo and B (Reactions (4)–(6)) are all negative as can be seen in Fig. 4b [26], thus formation of molybdenum borides is expected to take place by Reactions (4)–(6). The reason for the incomplete occurrence of Reactions (4)–(6) can probably be addressed to kinetic factors, i.e. the insufficient inter-diffusion rate of Mo or B.

$$2Mo + B = Mo_2B \qquad (4)$$

$$Mo + B = MoB \qquad (5)$$

$$Mo + 2B = MoB_2 \qquad (6)$$

3.2. Mechanochemical synthesis (MCS) and annealing

In the first experiment, reactants were ball milled for 13 h. The presence of localized melting, observed after the experiment on the rubber seal of the jar was taken as an indication that the reaction occurred with an explosive behavior and a sudden release of hot gas from the jar. The same result was obtained and reaction was seen to have occurred when ball milling was conducted for 8 h or 5 h.

XRD pattern of the product obtained by MCS is given in Fig. 5a. It can be seen that the product was composed of MgO, Mo, and a
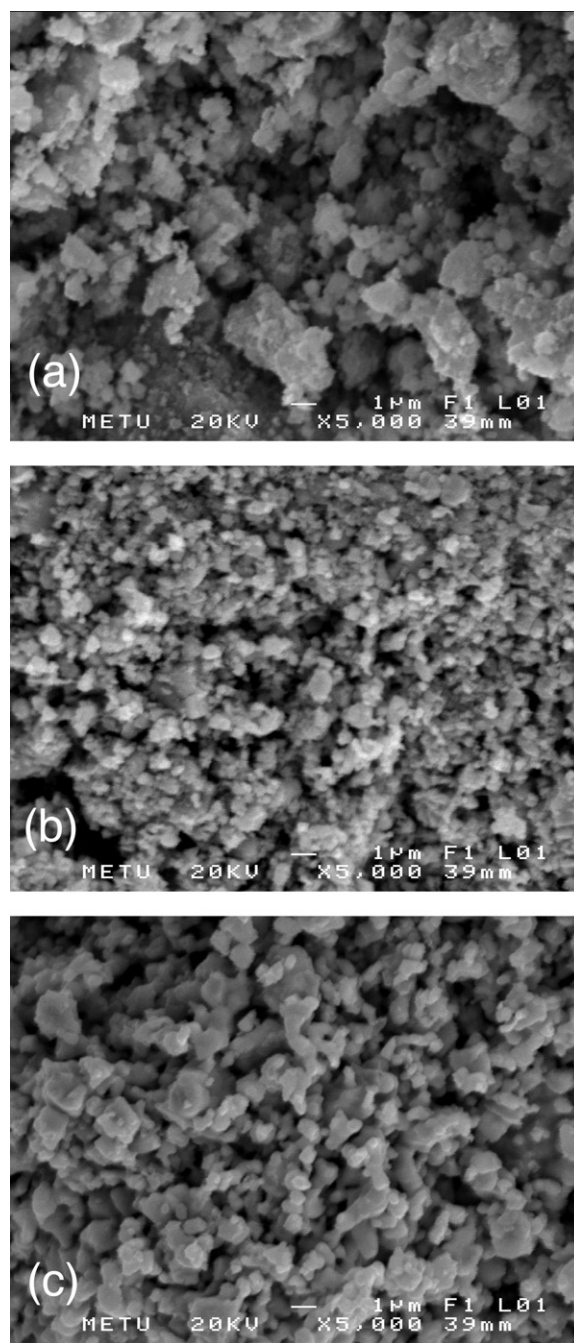

Fig. 6. SEM micrographs of the products obtained after (a) MCS, (b) leaching MCS products and (c) annealing the leached product under argon at 1400 °C for 3 h.

mixture of borides: Mo$_2$B, MoB and MoB$_2$. The expected reaction products were MoB and MgO.

Magnesium borate was not present in the products of MCS, while it was found as a side product in VCS. The absence of magnesium borate in the products was reported to be an advantage of the MCS technique, since the leaching process of magnesium borate is a time consuming process [6]. MCS products contained, besides MoB, Mo and also lower boride species (Mo$_2$B) and higher boride species (MoB$_2$), than MoB. Thus, equal molar ratio of Mo and B is believed to be maintained in the products. MoB$_2$, which is present in the MCS products, is stable at temperatures higher than 1517 °C, according to the phase diagram given in Fig. 1. MoB$_2$ may have formed due to the fact that non-equilibrium compounds can form by MCS [24]. In other studies in literature, formation of MoB$_2$ was observed during

milling or in subsequent annealing of elemental Mo and B powders [17,25].

It was seen in SEM examinations that the product obtained after MCS was composed of agglomerates in 10–20 μm size. An SEM micrograph showing the structure of an agglomerate is presented in Fig. 6a. Particles inside the agglomerates were smaller than 0.5 μm, although there were larger formations having a few micrometer sizes.

In order to remove MgO, MCS products were leached for 30 min in 1 M HCl solution. According to the XRD pattern presented in Fig. 5b, the leached product was composed of Mo, Mo_2B, MoB and MoB_2. The same results were obtained by leaching the milled products of the repeated experiments. During the leaching step of MgO, the agglomerates were broken up and particles were liberated. Particles consisting of a mixture of boride phases can be seen in the SEM micrograph given in Fig. 6b. After the removal of MgO, the particle size was seen to be below 0.5 μm.

Formation of boride phases according to the ratio of Mo and B in the reactants was reported to occur during the annealing process, which was preformed after ball milling of Mo and B powders [17]. Therefore, the leached product obtained in the present study was pressed in the form of a pellet and annealed under argon atmosphere at 1400 °C in a tube furnace. Mo is not stable in the presence of B, since the free energies of formation of molybdenum borides are highly negative, as shown in Fig. 4b [27]. It is thermodynamically expected that Mo, and lower boride phases such as Mo_2B, react with higher boride phases such as MoB_2 to produce MoB (Reactions (7) [1] and (8)). The free energies of Reactions (7) and (8) are in fact also negative [27], as presented in Fig. 4b. It can be seen in the Mo–B phase diagram given in Fig. 1 that, from room temperature up to 1517 °C there is no temperature dependent phase transformation. Therefore, 1400 °C is believed to be a suitable temperature to obtain the stable boride phase by solid state diffusion of Mo and B, in accordance with the stoichiometry of the species in the mixture of borides.

$$Mo + MoB_2 = 2MoB \tag{7}$$

$$Mo_2B + MoB_2 = 3MoB \tag{8}$$
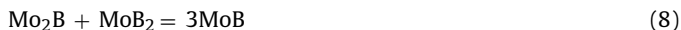
XRD pattern of the annealed sample is presented in Fig. 5c. After annealing at 1400 °C, the leached product, which was composed of a mixture of borides, was converted into single phase α-MoB. Molybdenum boride particles were seen to grow as a result of the annealing process. Size of MoB particles was much larger (Fig. 6c) than the particles in the leached product given in Fig. 6b. The size of MoB particles was estimated to be smaller than 1 μm after annealing. Some particles fused to each other due to thermal treatment.

4. Conclusions

Formation of molybdenum monoboride was investigated by volume combustion process from $MoO_3 + B_2O_3 + Mg$ mixtures. Mo and a mixture of boride phases were seen to form even when diluents and excess amounts of B_2O_3 and Mg were used. It was suggested that incomplete formation of molybdenum boride was probably caused by the insufficient diffusion of Mo and B species during volume combustion. Reactant mixtures having the same composition as in VCS were subjected to mechanochemical synthesis. MCS products were composed of Mo and a mixture of boride phases. Single phase α-MoB was obtained after annealing the MCS products at 1400 °C.

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