



# Preparation of single phase molybdenum boride

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## ARTICLE INFO

### Article history:

Received 14 October 2010

Received in revised form 13 February 2011

Accepted 16 February 2011

Available online 23 February 2011

### Keywords:

Solid state reactions

Mechanochemical synthesis

Volume combustion synthesis

Molybdenum borides

MoB

## ABSTRACT

The formation of MoB through volume combustion synthesis (VCS), and through mechanochemical synthesis (MCS) followed by annealing has been investigated.  $\text{MoO}_3$ ,  $\text{B}_2\text{O}_3$  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.  $\text{Mo}_2\text{B}$ , MoB,  $\text{MoB}_2$  and  $\text{Mo}_2\text{B}_5$  were found as minor phases. Products of MCS contained a mixture of  $\text{Mo}_2\text{B}$ , MoB,  $\text{MoB}_2$  and Mo. After annealing the MCS product at  $1400^\circ\text{C}$  for 3 h, single phase  $\alpha$ -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  $\text{TiB}_2$  or  $\text{TiB}$  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– $\text{MoSi}_2$  or  $\text{Mo}_2\text{B}_5$ – $\text{MoSi}_2$  compositions have been used as oxidation resistant composites [14] or coatings [2,15]. The Mo–B phase diagram (Fig. 1) contains 5 phases:  $\text{Mo}_2\text{B}$ , MoB,  $\text{MoB}_2$ ,  $\text{Mo}_2\text{B}_5$  and  $\text{Mo}_{1-x}\text{B}_3$  ( $\text{MoB}_4$ ) [16]. MoB exists in two allotropic forms:  $\alpha$ -MoB is the low temperature phase having orthorhombic crystal structure and a solubility range of about 48.5–50.5 at% B;  $\beta$ -MoB is stable above  $1800^\circ\text{C}$ , 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 (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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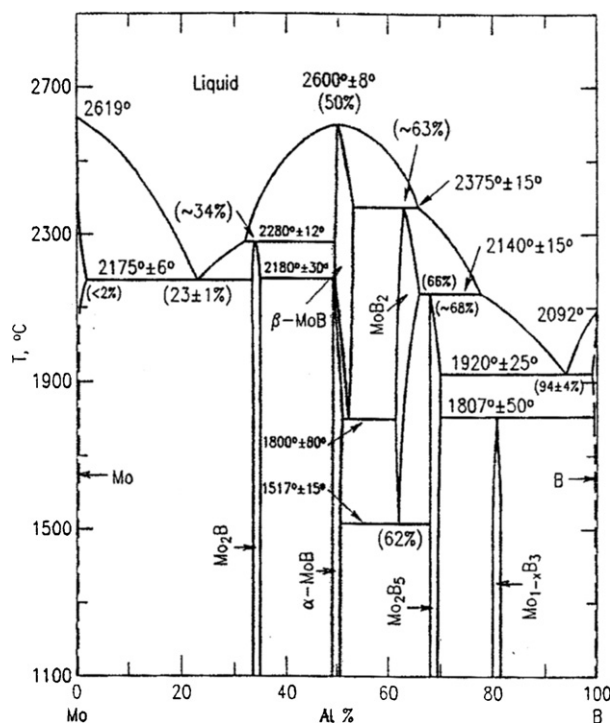


Fig. 1. Mo–B phase diagram [16].

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  $\text{MoO}_3$  and  $\text{B}_2\text{O}_3$ . For this purpose, the volume combustion method as well as a combined method of mechanochemical synthesis and thermal treatment was examined.

**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 $\text{MoO}_3$ , Mo, B [19] Mo, B, Si [2]	$\alpha$ -MoB $\text{Mo}_2\text{B}$ $\text{MoB}_2$ $\text{Mo}_2\text{B}_5$ $\text{MoB}_4$ $\alpha$ -MoB, $\text{MoSi}_2$	$\alpha$ -MoB, $\text{Mo}_2\text{B}$ $\text{Mo}_2\text{B}$ , Mo, $\alpha$ -MoB $\text{MoB}_2$ , $\alpha$ -MoB, $\beta$ -MoB, $\text{Mo}_2\text{B}_5$ $\text{MoB}_2$ , $\text{Mo}_2\text{B}_5$ , $\alpha$ -MoB $\text{Mo}_2\text{B}_5$ , $\text{MoB}_4$ $\alpha$ -MoB, $\beta$ -MoB, $\text{MoSi}_2$ , $\text{Mo}_5\text{Si}_3$	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	$\text{MoB}_2$ $\text{Mo}_2\text{B}_5$	Mo, $\text{MoB}_2$ (after milling), $\text{MoB}_2$ , $\text{Mo}_2\text{B}_5$ (after annealing) $\text{Mo}_2\text{B}_5$ (after annealing)	Single phase $\text{Mo}_2\text{B}_5$ was obtained.
MCS [25]	Ball milling then annealing at 1400 °C	Mo, B, Si	Mo/ $\text{Mo}_5\text{SiB}_2$	Mo, $\text{Mo}_2\text{B}$ , MoB, $\text{MoB}_2$ , besides silicides	Direct synthesis of Mo and $\text{Mo}_5\text{SiB}_2$ 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	$\text{MoO}_3$ , $\text{KBH}_4$ and $\text{CCl}_4$	$\alpha$ -MoB	Mo, $\alpha$ -MoB	A mixture of boride phases and Mo formed after hydrothermal synthesis. After annealing at 900 °C, Mo and MoB formed. Although $\text{KBH}_4$ to $\text{MoO}_3$ ratio was 6, MoB having equimolar Mo and B formed.

## 2. Experimental procedures

$\text{MoO}_3$  (Merck, purity >99.5%) +  $\text{B}_2\text{O}_3$  + Mg (Aldrich, –50 mesh, purity >99%) mixtures containing excess amounts of Mg and  $\text{B}_2\text{O}_3$  were prepared according to the stoichiometry of Reaction (1). In this reaction  $\text{MoO}_3$  and  $\text{B}_2\text{O}_3$  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.  $\text{B}_2\text{O}_3$  was produced by calcination of  $\text{H}_3\text{BO}_3$  (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].



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  $3.33 \times 10^{-5} \text{ m}^3/\text{s}$ ). 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  $\text{Cu-K}\alpha$  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  $\text{MoO}_3$  + Mg +  $\text{B}_2\text{O}_3$  mixture

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