Preparation of MoB and MoB–MoSi$_2$ composites by combustion synthesis in SHS mode

C.L. Yeh *, W.S. Hsu

Department of Mechanical and Automation Engineering, Da-Yeh University, 112 Shan-Jiau Road, Da-Tsuen, Changhua 51505, Taiwan

Abstract

Combustion synthesis in the mode of self-propagating high-temperature synthesis (SHS) was carried out in the Mo–B and Mo–B–Si systems for the preparation of molybdenum boride MoB and the composite of MoB–MoSi$_2$ from elemental powder compacts. Under a preheating temperature above 150 °C, the reaction of Mo with boron in the sample compact of Mo:B = 1:1 is characterized by a planar combustion front propagating in a self-sustaining and steady manner. As the preheating temperature or sample compaction density increased, combustion temperature was found to increase and the propagation rate of the combustion front was correspondingly enhanced. Moreover, the XRD analysis provides evidence of yielding nearly single-phase α-MoB from the Mo–B sample at equiatomic stoichiometry. In the synthesis of MoB–MoSi$_2$ composites, the starting stoichiometry of the Mo–B–Si powder compact was varied so as to produce the final composites containing 20–80 mol% MoB. It was also found the increase of flame-front velocity and combustion temperature with increasing MoB content formed in the composite. The composition analysis by XRD shows excellent conversion from the Mo–B–Si powder compact to the MoB–MoSi$_2$ composite through the SHS reaction; that is, in addition to a small amount of Mo$_5$Si$_3$, the as-synthesized composite is composed entirely of MoB and MoSi$_2$.
© 2006 Elsevier B.V. All rights reserved.

Keywords: MoB; MoB–MoSi$_2$ composite; SHS; Preheating temperature; XRD

1. Introduction

Preparation of various boride compounds in the Ti–B, Zr–B, Hf–B, Nb–B, and Ta–B systems by self-propagating high-temperature synthesis (SHS) has been demonstrated in a number of investigations [1–10]. Under the SHS mode of combustion synthesis, metal borides can be produced by the direct reaction of constituent elements or by the reaction of metal oxides with boron [10]. The latter approach is used for cases in which a direct combustion reaction between the metal and boron is not feasible. Combustion synthesis takes advantage of the self-sustaining merit from the highly exothermic reaction of powder constituents and hence has the potential of cost reduction, low energy requirement, and yielding of high purity products. This technique has been extensively employed to produce a variety of advanced materials, including borides, carbides, nitrides, hydrides, aluminides, silicides, intermetallics, etc. [10–14].

Among the transition metal borides formed by SHS, titanium diboride TiB$_2$ was the most studied compound [1–5]. Lately, Yeh and Chen [8,9] conducted a comparative study on combustion synthesis of different phases of niobium borides (including Nb$_3$B$_2$, NbB, Nb$_5$B$_6$, Nb$_3$B$_4$ and NbB$_2$) from elemental powder compacts with corresponding stoichiometries. However, little information is available on the formation of molybdenum borides by SHS in the literature. The phase diagram of the Mo–B binary system [15] shows the presence of five boride phases: Mo$_2$B, MoB, MoB$_2$, Mo$_2$B$_5$ and MoB$_4$, but the diboride MoB$_2$ only exists at temperatures above 1500 °C. When preparing molybdenum borides by SHS, Zenin et al. [7] reported that the self-sustaining reaction was only achieved in the sample with a starting stoichiometry of Mo:B = 1:1 and the combustion wave propagated in a pulsating mode. Formation of other boride phases of molybdenum was suggested by means of solid-state displacement reactions between molybdenum oxide (MoO$_3$), Mo, and B [10].

Due to the high melting points (2600, 2375, and 2140 °C for MoB, MoB$_2$ and Mo$_2$B$_5$, respectively), chemical stability, extremely high hardness, good corrosion resistance, and

---

* Corresponding author. Tel.: +886 4 8511888x2118; fax: +886 4 8511215.
  E-mail address: clyeh@mail.dyu.edu.tw (C.L. Yeh).

excellent high-temperature strength, molybdenum borides have attracted considerable interest for structural applications [16]. Additionally, the Mo–B–Si ternary system indicates that at least two of the molybdenum borides, namely MoB and Mo_2B_5, are in equilibrium with $MoSi_2$ at temperature around 1600 °C [17,18]. Besides the aforementioned properties, MoB and Mo_2B_5 have good thermal conductivity and relatively high coefficients of thermal expansion, which makes them promising candidates for reinforcing $MoSi_2$ [17]. Preparation of $MoSi_2$–MoB and $MoSi_2$–Mo_2B_5 composites was attempted by Costa e Silva and Kaufman [17,18] through in situ displacement reactions of a Mo-rich silicide Mo_5Si_3 with boron. Their results showed that the grain sizes of the silicide and the boride were substantially finer in the composite containing MoB than that with Mo_2B_5 [17,18].

The objective of this study was to investigate formation of molybdenum monoboride MoB and the composite of MoB–$MoSi_2$ by the SHS method using compacted samples from Mo–B and Mo–B–Si elemental powder mixtures, respectively. In the synthesis of monolithic MoB, effects of the initial sample density and preheating temperature were studied on combustion characteristics. Moreover, the activation energy associated with combustion synthesis of MoB was determined by correlating the temperature dependence of combustion wave velocity. In the case of preparing MoB–$MoSi_2$ composites with a broad range of compositions, the starting stoichiometry of the reactant compact was varied and its corresponding effects on the reaction front velocity, combustion temperature, and degree of conversion were addressed.

2. Experimental methods of approach

Elemental powders used in this study as the starting materials include molybdenum (Strem Chemicals, 3–7 μm, 99.9% purity), boron (Noah Technologies Corp., about 1 μm, 92% purity), and silicon (ProChem Inc., <45 μm, 99.5% purity). For the preparation of molybdenum monoboride, Mo and B powders at equiatomic stoichiometry were dry mixed in a ball mill for 10 h. Mixed powders then contained in a stainless-steel mold were uniaxially pressed at pressures of about 50–70 MPa into cylindrical samples (having a diameter of 7 mm and a height of 12 mm) with density ranging from 40 to 50% of the theoretical value, which is 7.69 g/cm³ for the powder mixture with Mo:B = 1:1. The influence of

initial sample temperature was studied by performing the experiments at different sample preheating temperatures (T_p) from room temperature to 400 °C.

In the case of producing MoB–$MoSi_2$ composites, reactant compacts consisting of Mo, B, and Si at different atomic ratios were prepared according to the following reaction:

$$Mo + xB + 2(1 - x)Si \rightarrow xMoB + (1 - x)MoSi_2 \qquad (1)$$
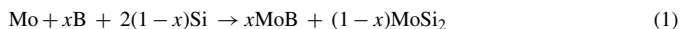
In Reaction (1), the coefficient x represents the amount of boron with respect to Mo in the reactant compact and also signifies the mole fraction of MoB in the MoB–$MoSi_2$ composite. The value of x varies between 0.2 and 0.8 in this study. Additionally, every Mo–B–Si powder compact was formed with a packing density at 55% of the theoretical value and ignited at a preheating temperature of 300 °C. The theoretical density (TD) of the Mo–B–Si mixture depends upon the composition and varies between 6.2 and 5.9 g/cm³ with $x = 0.2$–0.8. For example, the powder mixture of Mo + 0.2B + 1.6Si has a TD 6.2 g/cm³, and the Mo + 0.8B + 0.4Si mixture has a TD 5.9 g/cm³.

The SHS experiments were conducted in a stainless-steel windowed combustion chamber under an atmosphere of high purity argon (99.99%). In order to ensure the initiation of self-sustaining reactions, a compacted pellet (2 mm in height and 7 mm in diameter) made up of titanium (Ti) and carbon black (C) (with a molar ratio Ti:C = 1:1) was placed on the top of the test specimens to serve as an ignition enhancer which was triggered by a heated tungsten coil. Details of the experimental setup and measurement approach were previously reported [19,20]. After combustion, the composition of as-synthesized products was identified by an X-ray diffractometer (Shimadzu XRD-6000) operating with Cu Kα radiation.

3. Results and discussion

3.1. Observation of combustion characteristics

Experimental observations showed that the stability of the self-propagating reaction in the Mo + B powder compact was influenced by the initial sample density and temperature. Fig. 1 presents a recorded combustion process associated with formation of monolithic MoB from a 50% TD sample compact at $T_p = 300$ °C. As illustrated in Fig. 1, upon ignition a planar reaction front develops and traverses the entire sample in a self-sustaining and steady manner. However, it should be noted that the planar reaction front was no longer stable in the Mo–B samples without prior heating or compressed at a lower density like 40% TD, under which combustion was confined to a localized reaction zone propagating along a spiral trajectory.
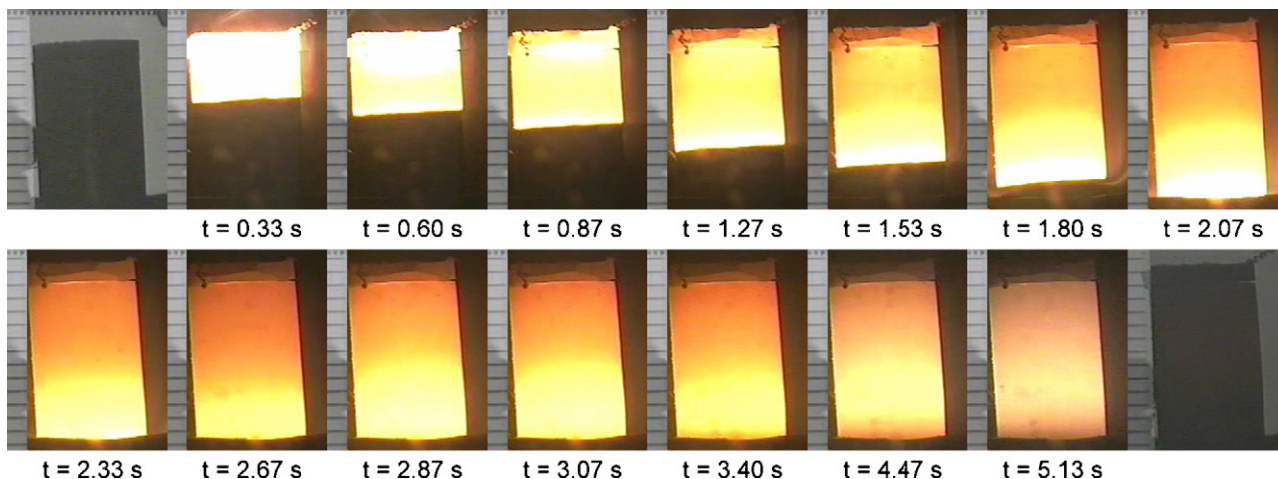

t = 0.33 s   t = 0.60 s   t = 0.87 s   t = 1.27 s   t = 1.53 s   t = 1.80 s   t = 2.07 s

t = 2.33 s   t = 2.67 s   t = 2.87 s   t = 3.07 s   t = 3.40 s   t = 4.47 s   t = 5.13 s

Fig. 1. Recorded combustion images associated with formation of monolithic MoB from a 50% TD powder compact of Mo:B = 1:1 at $T_p = 300$ °C.