Effects of excess boron on combustion synthesis of alumina–tantalum boride composites

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Abstract

TaB- and TaB$_2$–Al$_2$O$_3$ in situ composites were fabricated by thermite-incorporated combustion synthesis from the powder mixtures of different combinations, including Ta$_2$O$_5$–Al–B, Ta$_2$O$_5$–Al–B$_2$O$_3$–B, and Ta$_2$O$_5$–B$_2$O$_3$–Al. Effects of excess boron were studied on the combustion dynamics and phase constituents of final products. For the B$_2$O$_3$-containing samples, the reaction was less exothermic and aluminothermic reduction of Ta$_2$O$_5$ and B$_2$O$_3$ was less complete, resulting in the deficiency of boron and the presence of TaO$_2$ and Ta. For the samples containing elemental boron, the occurrence of borothermic reduction of Ta$_2$O$_5$ also caused the loss of boron. Experimental evidence showed that boron in excess of the stoichiometric amount substantially enhanced the formation of tantalum borides, which in turn facilitated the reduction of Ta$_2$O$_5$ by Al. Consequently, the samples rich with boron in the molar proportions of Ta$_2$O$_5$:Al:B $=3$:10:9 and 3:10:16 (i.e., B/Ta $=1.5$ and 2.67) were found to be the optimum stoichiometries of producing TaB- and TaB$_2$–Al$_2$O$_3$ composites through a self-sustaining combustion process.
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1. Introduction

Transition metal (Groups IVb and Vb) borides, such as TiB$_2$, ZrB$_2$, HfB$_2$, TaB$_2$, etc., have attracted great attention because of their unique combination of many favorable properties, including high melting temperatures, high hardness, good chemical stability, high electrical and thermal conductivity, and good wear and corrosion resistance [1–3]. The combination of properties makes these materials potential candidates for a variety of high-temperature applications, including engines, rocket motor nozzles, plasma arc electrodes, cutting tools, ballistic armors, and furnace elements [4]. Moreover, many reinforcing additives such as Al$_2$O$_3$ [5,6], ZrO$_2$ [7], TiC [8], and SiC [9,10] have been incorporated to improve the mechanical properties of various transition metal borides and carbides.

For the formation of high temperature materials, combustion and plasma synthesis are two important fabrication routes [11–13]. Combustion synthesis, particularly in the mode of self-propagating high-temperature synthesis (SHS), takes advantage of the intense energy release from highly exothermic reactions, and hence, has the merits of high energy efficiency, simplicity, high productivity, structural and functional diversity of final products, etc. [14,15]. Furthermore, combustion synthesis involving aluminothermic reduction of metal oxides (i.e., the thermite reaction) represents an in situ technique for producing composite materials with the addition of Al$_2$O$_3$ [16,17]. Considerable exothermicity of the thermite reaction is beneficial for the SHS process, and the use of metal oxides as the starting materials instead of metallic elements is often cost-effective [18,19].

In view of the extremely high melting temperatures above 3000 °C for tantalum borides (TaB and TaB$_2$), composite materials based on TaB and/or TaB$_2$ are particularly promising for the ultra high-temperature applications. Although the formation of tantalum borides by SHS is feasible from the elemental powder compacts [20], both reagents are rather costly. Therefore, it is worthwhile to employ less expensive Ta$_2$O$_5$ and B$_2$O$_3$ as reactants in a thermite-based SHS process for the formation of TaB- and TaB$_2$–Al$_2$O$_3$ in situ composites.

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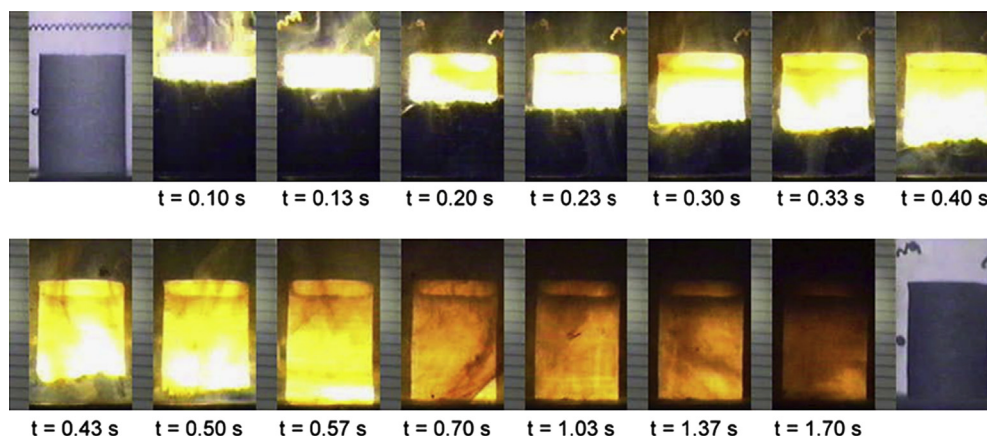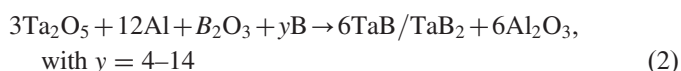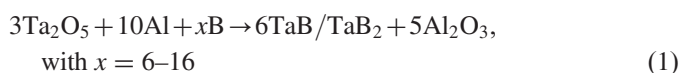fax: +886 4 2451 0862.
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Fig. 1. Recorded SHS sequences illustrating self-sustaining combustion along a powder compact of $3Ta_2O_5+10Al+xB$ with $x=15$.

In order to resolve the boron-deficient problem [21,22], the samples with excess boron were conducted in this study. Moreover, the effects of excess boron on the combustion temperature, reaction front velocity, and boride phases formed in the final products are investigated.

2. Experimental methods of approach

The starting powders adopted by this study included Ta_2O_5 (Strem Chemicals, 99.9%), B_2O_3 (Strem Chemicals, 99.9%), Al (Showa Chemical Co., $<45\ \mu m$, 99.9%), and amorphous boron (Noah Technologies Corp., $<1\ \mu m$, 92% purity). The first type of the reaction system expressed in Reactions (1) and (2) was designed to contain amorphous boron and to study the effect of excess boron.

$$3Ta_2O_5+10Al+xB\rightarrow 6TaB/TaB_2+5Al_2O_3,$$
$$\text{with } x=6\text{--}16 \qquad\qquad\qquad (1)$$

$$3Ta_2O_5+12Al+B_2O_3+yB\rightarrow 6TaB/TaB_2+6Al_2O_3,$$
$$\text{with } y=4\text{--}14 \qquad\qquad\qquad (2)$$

The reactant mixture of Reaction (1) comprises Ta_2O_5, Al, and B powders under a molar proportion of $3Ta_2O_5+10Al+xB$ with $x=6$–16. In Reaction (1), aluminothermic reduction of Ta_2O_5 produces Ta and Al_2O_3, and the reduced Ta reacts subsequently with boron. As the parameter x exceeds the stoichiometric values for the synthesis of TaB and TaB_2 (i.e., $x=6$ and 12, respectively), the SHS process is considered to proceed with excess boron.

Reaction (2) employs two oxide reagents, Ta_2O_5 and B_2O_3, to mix with Al and boron in the composition of $3Ta_2O_5+12Al+B_2O_3+yB$ with $y=4$–14. The role of B_2O_3 in Reaction (2) is the other source of boron. That is, co-reduction of Ta_2O_5 and B_2O_3 by Al is required. Similar to Reaction (1), the effect of excess boron is studied by Reaction (2), where $y=4$ signifies the exact stoichiometric condition for the formation of TaB and $y=10$ for that of TaB_2.

The second type of the reactant mixture is free of amorphous boron and adopts B_2O_3 as the only supply of boron. Reactions (3) and (4) are intended to produce TaB- and TaB_2–Al_2O_3

composites, respectively, from the mixtures of Ta_2O_5, B_2O_3, and Al powders.

$$3Ta_2O_5+3B_2O_3+16Al\rightarrow 6TaB+8Al_2O_3 \qquad (3)$$

$$3Ta_2O_5+6B_2O_3+22Al\rightarrow 6TaB_2+11Al_2O_3 \qquad (4)$$

The reactant powders with designed compositions were dry mixed in a ball mill and then cold-pressed into the cylindrical samples with a diameter of 7 mm, a height of 12 mm, and a compaction density of 50% relative to 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 previously reported [23]. In addition, Vickers hardness (H_v) and fracture toughness (K_{IC}) of the synthesized composites were evaluated [24].

3. Results and discussion

3.1. Measurement of flame-front propagation velocity

Fig. 1 shows a typical combustion process recorded from Reaction (1) with $x=15$. It is evident that a distinct combustion front forms upon ignition and propagates along the sample in a self-sustaining manner. As clearly revealed in Fig. 1, the progression of the combustion wave is accompanied with visible smoke, implicative of the formation of gaseous products or an aerosol of solid or liquid particulates. It is believed that a certain degree of borothermic reduction of Ta_2O_5 occurred and led to the yield of gaseous BO and molten B_2O_3, both of which were then expelled from the porous sample. This was subsequently responsible for the lack of boron to form tantalum borides.

The propagation velocity (V_f) of the combustion front was determined from the recorded SHS images. As presented in Fig. 2, the flame-front velocity is affected not only by the atomic ratio of B/Ta of the reactant mixture, but also by the use of B_2O_3 as the reagent. With the increase of the boron content of Reaction (1) from B/Ta=1.0 to 2.67 (i.e., $x=6$–16), the combustion wave velocity increases from 16.1 mm/s to a peak