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Formation of WB_2/mullite composites by reduction-based combustion synthesis with Al and Si as reductants and excess B_2O_3 addition

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ABSTRACT

Fabrication of WB_2/mullite composites was conducted by combustion synthesis involving metallothermic reduction of WO_3 and B_2O_3 in the mode of self-propagating high-temperature synthesis (SHS). Effects of excess B_2O_3 and pre-added and in situ formed SiO_2 on formation of boride and mullite were investigated. Powder compacts with pre-added SiO_2 were composed of $xWO_3+yB_2O_3+6Al+2SiO_2$ with y/x=1.0–2.0. For the Si-containing samples, the starting mixtures comprised $mWO_3+nB_2O_3+6Al+2Si$ with n/m=1.0–2.0. The Si-adopted samples are more exothermic than the SiO_2-added samples, and the reaction temperature and combustion wave velocity decreases with increasing molar proportion of B_2O_3/WO_3. The phase evolution was improved by adding excess B_2O_3 to compensate for its evaporation loss during the SHS process. As a result, the intermediates WB and WSi_2 were significantly reduced in the final WB_2/mullite composite of the SiO_2-added sample with excess B_2O_3 of y/x=2.0. With the advantage of using Al and Si as reductants, the Si-based reaction of n/m=1.75 produced a WB_2/mullite composite with negligible WB and WSi_2.

1. Introduction

Mullite is a stable solid solution phase in the Al_2O_3–SiO_2 system. Mullite ($3Al_2O_3{\cdot}2SiO_2$) not only is a promising high-temperature structural material but also is a candidate for use in the electronic packing and optical applications, due to its unique properties including high melting point, high creep resistance, excellent thermal stability, good chemical resistance, good thermal shock resistance, low thermal expansion coefficient, low dielectric constant, and transmittance to infrared [1–3]. Additionally, mullite-based composites with ZrO_2 and Al_2O_3 as reinforcements possess improved fracture toughness, flexural strength, corrosion resistance, and thermal shock resistance, and therefore, have been broadly studied [4–8]. Considerable attention has recently been paid to mullite combined with other ceramic and intermetallic additives, such as TiC, SiC, TiB_2, TaB_2, BN, Al_2TiO_5, and $MoSi_2$ [9–15].

A variety of processing methods with different starting materials have been employed to prepare mullite in a monolithic or composite form. Fabrication techniques comprise reaction sintering [4,16], spark plasma sintering (SPS) [5,9], self-propagating high-temperature synthesis (SHS) [11,12], thermal explosion [15], sol-gel method [17,18], gel casting [19,20], and solution combustion synthesis [21,22]. Combustion synthesis of the SHS mode takes advantage of highly exothermic reactions, and hence, is an energy-efficient and time-saving production route [23–25]. The SHS method has other merits like high productivity, simplicity, high-purity products, and a diversity of final products. A large number of transition metal (mostly the groups IVb and Vb) borides have been produced by the SHS process from the elemental powder compacts of their corresponding stoichiometries [25–28]. However, direct combustion between the group-VIb transition metals (Cr, Mo, and W) and boron is not feasible. An alternative approach of preparing Cr–B, Mo–B, and W–B compounds is based upon metallothermic reduction of respective metal oxides, Cr_2O_3, MoO_3, and WO_3 [25]. By incorporating borothermic reduction of WO_3 into the W–B combustion system, tungsten borides of different phases were produced in the SHS manner [29]. Yazici and Derin [30] performed the SHS reaction involving magnesiothermic reduction of WO_3 and B_2O_3 to fabricate WB and W_2B_5. In addition, Nasiri-Tabrizi et al. [31] obtained WB–W_2B_5–MgO composites from the WO_3/B_2O_3/Mg mixture through mechanochemically induced self-sustaining reaction.

When Al is used as the reductant, aluminothermic reduction of WO_3 not only is highly energetic but produces Al_2O_3. Generation of a large amount of heat is a great benefit for combustion synthesis and Al_2O_3 is one of two constituents of mullite. Therefore, this study aims to fabricate WB_2/mullite composites by reduction-based combustion synthesis involving aluminothermic reduction of WO_3 and B_2O_3. With regard to the source of boron, the use of B_2O_3 instead of elemental

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Table 1
Molar contents of WO_3 and B_2O_3 in Reactions (1) and (2).

Molar Ratio of B_2O_3/WO_3 (y/x and n/m)	Reaction (1)		Reaction (2)	
	x	y	m	n
1.0	3/2	3/2	13/6	13/6
1.25	4/3	5/3	52/27	65/27
1.5	6/5	9/5	26/15	39/15
1.75	12/11	21/11	52/33	91/33
2.0	1	2	13/9	26/9

boron is cost-effective. Besides Al, this study employs Si as the second reducing agent in order to compare the effects of in situ formed SiO_2 with pre-added SiO_2 on mullite formation and combustion behavior. Because of high volatility of B_2O_3 at elevated temperatures and possible outflowing of gaseous boron oxides (e.g., BO and B_2O_2) generated from reduction of B_2O_3, excess B_2O_3 is a subject of importance to compensate for the loss of boron. According to Guo and Zhang [32,33], B_2O_3 has a high vapor pressure reaching up to 344 Pa at 1527 °C, which leading to its rapid vaporization. Ran et al. [34] also indicated that at above 1200 °C, $B_2O_{2(g)}$ and $BO_{(g)}$ started to form from a reaction between B_2O_3 and B or by the gas-phase decomposition of $B_2O_{3(g)}$. Therefore, this study adopts excess B_2O_3 in the reactant mixture and investigates its influence on evolution of WB_2 and combustion characteristics.

2. Experimental methods of approach

The starting materials of this study include WO_3 (Alfa Aesar, 99.8%), B_2O_3 (Strem Chemicals, 99.9%), Al (Showa Chemical Co., < 45 μm, 99.9%), SiO_2 (Strem Chemicals, 99%), and Si (Strem Chemicals, < 45 μm, 99%). Two reaction systems with different mullite formation mechanisms were conducted. Reaction (1) adopts Al as the reducing agent for WO_3 and B_2O_3 and is formulated with pre-added SiO_2. Formation of mullite from pre-added SiO_2 and redox-produced Al_2O_3 was studied in Reaction (1).

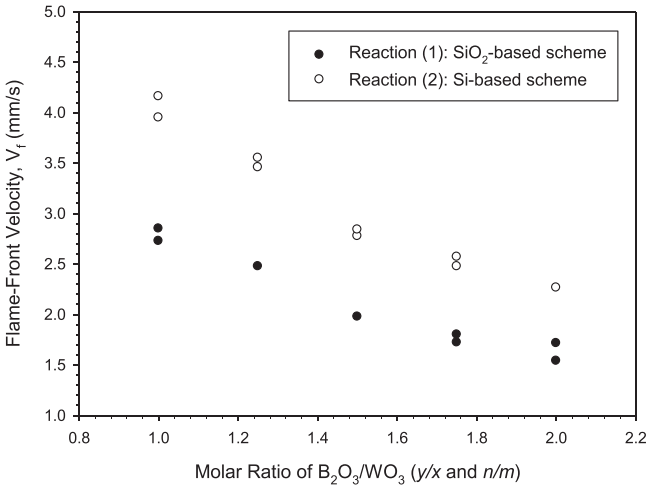

Fig. 2. Effects of molar ratio of B_2O_3/WO_3 on flame-front velocity of SiO_2- and Si-based reaction systems.

$$xWO_3 + yB_2O_3 + 6Al + 2SiO_2 \rightarrow \frac{3}{2}WB_2 + (3Al_2O_3{\cdot}2SiO_2) \quad (1)$$

where the stoichiometric coefficients, x and y, represent the mole

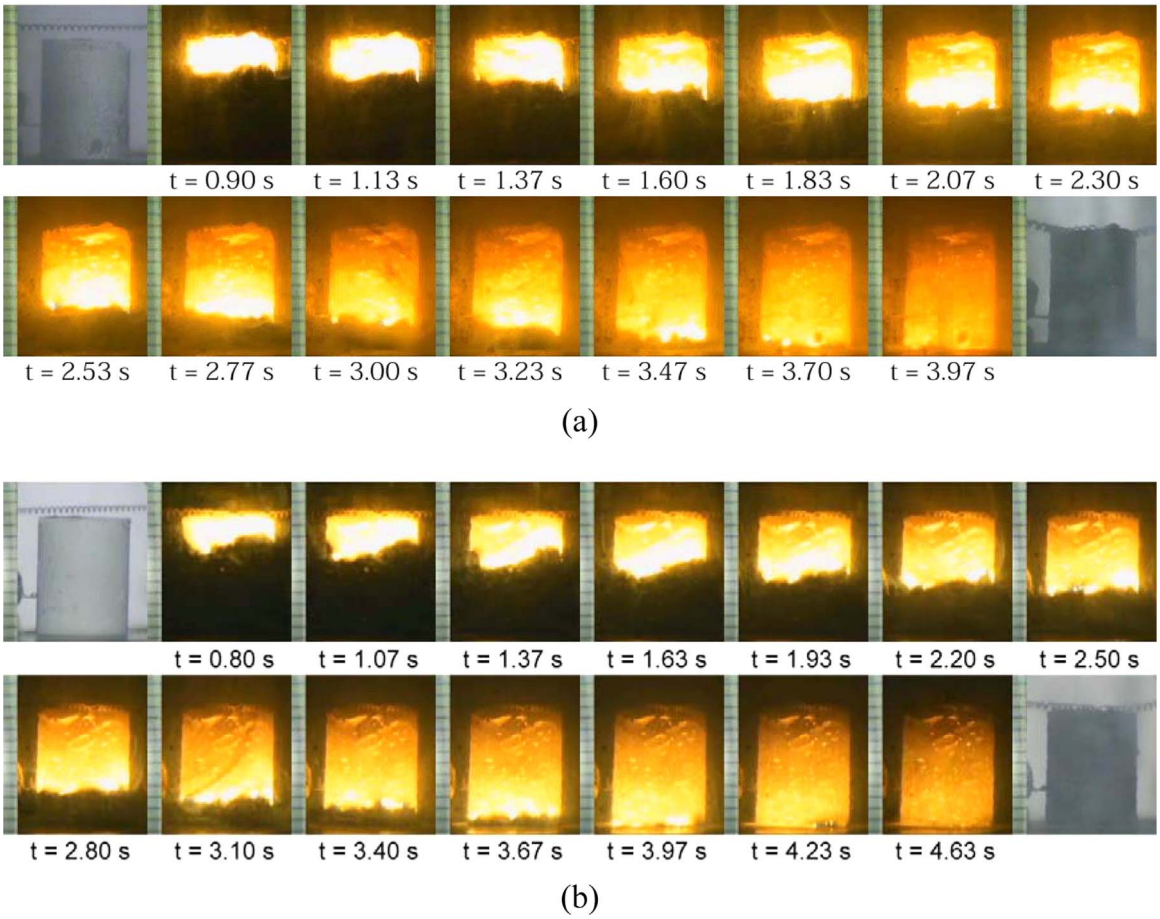

Fig. 1. Time sequences of recorded images illustrating self-sustaining combustion wave propagating along samples of (a) Reaction (1) with y/x=1.25 and (b) Reaction (2) with n/m=2.0.