



Formation of NbB₂/mullite composites by combustion synthesis involving metallothermic reduction of Nb₂O₅ and B₂O₃

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Abstract

NbB₂/mullite composites were fabricated by self-propagating high-temperature synthesis (SHS) involving metallothermic reduction of Nb₂O₅ and B₂O₃ by Al and Si. Two reactant mixtures formulated as 13/11Nb₂O₅+26/11B₂O₃+6Al+xSi with $x=2.0-3.0$ and 13/9Nb₂O₅+52/27B₂O₃+52/27B+6Al+ySi with $y=2.0-3.0$ were prepared to study the effect of in situ formed SiO₂ on combustion behavior and phase conversion. For comparison, test samples with pre-added SiO₂ were employed and they were composed of 6/5Nb₂O₅+B₂O₃+14/5B+6Al+2SiO₂, within which Al was the only reducing agent. When compared with combustion of the SiO₂-added sample, the SHS process of the Si-adopted sample was more exothermic and effective in reduction of B₂O₃. Moreover, metallothermic reduction of B₂O₃ was greatly improved for the samples with excess Si and their final products were NbB₂/mullite composites with negligible minor phases. However, due to incomplete reduction of B₂O₃ in the SiO₂-added sample, the resulting product consisted of mullite, three boride phases (NbB, Nb₃B₄, and NbB₂), and an amorphous compound.

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1. Introduction

Mullite is a stable solid solution compound in the Al₂O₃–SiO₂ system at atmospheric pressure. The stoichiometry of mullite ranges from relatively silica-rich 3Al₂O₃·2SiO₂ (3:2 mullite) to alumina-rich 2Al₂O₃·SiO₂ (2:1 mullite). The 3:2 composition has been the most studied mullite phase, which combines high melting point, high chemical and thermal stability, high creep and thermal shock resistance, low thermal expansion coefficient, low dielectric constant, and transmittance to infrared [1,2]. Mullite has been considered as an excellent candidate for use in high-temperature structural applications, as well as in the areas of electronics and optics [1,2]. Besides, extensive investigations have focused on mullite matrix composites reinforced by ZrO₂ and Al₂O₃, due to the improvement in fracture toughness, flexural strength, and thermal shock resistance [3–5]. Other ceramic

reinforcements, such as TiC, SiC, TiB₂, and MoSi₂, were also employed [6–9].

Various starting materials and fabrication routes have been applied to prepare mullite in either monolithic or composite form. The processing techniques include sol–gel method [10,11], slip casting [3,4], reaction sintering of mechanically-mixed powders [5,12,13], spark plasma sintering (SPS) [6,14], solution combustion synthesis [15,16], and self-propagating high-temperature synthesis (SHS) [8,17]. Combustion synthesis in the SHS mode is one of the emerging cost-effective technologies and is merited by high energy efficiency, short processing time, and simplicity. A variety of advanced materials, including carbides, borides, nitrides, silicides, and intermetallics such as aluminides and titanides, have been produced by the conventional and modified SHS methods [18,19]. When incorporated with the thermite reaction using Al as the reducing agent, the SHS process represents an in situ approach of fabricating ceramic and intermetallic matrix composites reinforced by Al₂O₃ [20,21].

According to the literature, the heat evolved from combustion reactions was utilized to support the endothermic mullitization

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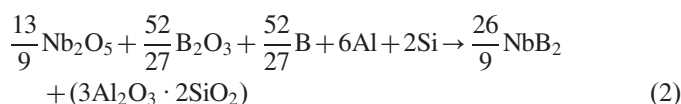
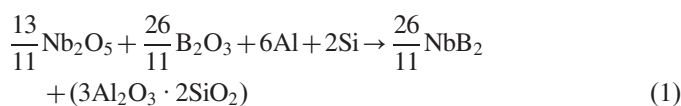
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process and allowed the mullite-based composite to be prepared in the SHS mode. With the addition of SiO₂ into a thermite mixture composed of TiO₂–B₂O₃–Al, Zaki [17] produced TiB₂/mullite composites by the SHS process under a preheating temperature of 550 °C on the sample compacts. Using the same technique at 600 °C of preheating, TiB₂/ZrO₂/mullite composites were obtained from the ZrSiO₄-added TiO₂–B₂O₃–Al powder blend [8]. Due to relatively weak exothermicity of the reaction system, the preparation of MoSi₂/mullite composites from the thermite mixture of MoO₃–SiO₂–Al was conducted by combustion synthesis in a thermal explosion mode with a resistance coil placed around the sample compact [9]. Because pre-added SiO₂ was adopted for formation of mullite, the dilution effect of SiO₂ on combustion and endothermic mullitization led to a need of prior heating on the sample or carrying out the reaction in a thermal explosion mode.

This study aims to fabricate NbB₂/mullite composites by combustion synthesis involving Nb₂O₅ and B₂O₃ subjected not only to aluminothermic but to silicothermic reduction. As a promising high-temperature structural material and a good reinforcing phase for mullite, niobium diboride (NbB₂) possesses high melting point, high hardness, high elastic modulus and mechanical strength, and excellent chemical and oxidation stability [22,23]. According to Jafari et al. [24], NbB₂ was synthesized from aluminothermic reduction in the Al–B₂O₃–Nb system via a mechanochemical process. In this study, the production of mullite from in situ formed SiO₂ and Al₂O₃ and the evolution of NbB₂ were investigated. Since the Si-added sample was utilized, the effect of the Si content was studied on combustion temperature, flame-front velocity, and product composition. In addition, the synthesis reaction of the SiO₂-containing sample employing Al as the only reductant was examined for comparison.

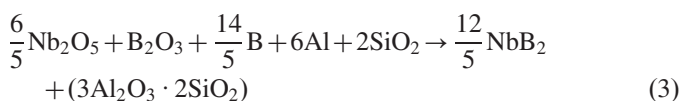
2. Experimental methods of approach

The starting materials utilized by this study included niobium (V) oxide (Nb₂O₅) (Strem Chemicals, < 45 μm, 99.9%), B₂O₃ (Strem Chemicals, 99.9%), SiO₂ (Strem Chemicals, 98%), Al (Showa Chemical Co., < 45 μm, 99.9%), Si (Strem Chemicals, < 45 μm, 99%), and amorphous boron (Noah Technologies Corp., < 1 μm, 92%). Reaction systems (1) and (2) were prepared to have both Al and Si as the reducing agents of Nb₂O₅ and B₂O₃. The starting stoichiometry of Reaction (1) is formulated as 13/11Nb₂O₅ + 26/11B₂O₃ + 6Al + xSi with x = 2.0–3.0. Reaction (2) contains elemental boron in addition to B₂O₃ to increase the content of NbB₂ and is composed of 13/9Nb₂O₅ + 52/27B₂O₃ + 52/27B + 6Al + ySi with y = 2.0–3.0. Reaction (1) with x = 2.0 and Reaction (2) with y = 2.0 represent their exact stoichiometric conditions and are expressed below



For Reaction systems (1) and (2), particular attention was paid to the non-stoichiometric samples containing up to 50 mol% Si in excess of the stoichiometric amount to compensate for the possible evaporation loss of Si during the SHS process.

On the other hand, the experiment was also conducted with SiO₂-adopted samples in order to realize the difference between pre-added and in situ formed SiO₂ in combustion synthesis of NbB₂/mullite composites. The degree of metallothermic reduction of Nb₂O₅ and B₂O₃ was compared between the use of one (Al) and two (Al and Si) reductants. Reaction (3) is associated with the SiO₂-added sample and is designed to have its final product with a similar composition to that of Reaction (1).



Test samples in a cylindrical shape with 7 mm in diameter, 12 mm in length, and 55% in relative density were obtained from pressing the well-mixed reactant powders in a die. Combustion synthesis was conducted under high-purity (99.99%) argon of 0.15 MPa. The combustion propagation rate and combustion temperature were precisely measured. Due to the extremely high intensity of light emission from the combustion reaction, the exposure time of each recorded image was set at 0.1 ms. To facilitate the accurate measurement of instantaneous locations of the combustion front, a beam splitter (Rolyn Optics), with a mirror characteristic of 75% transmission and 25% reflection, was used to optically superimpose a scale onto the image of the sample compact. Details of the experimental setup and diagnostic techniques were reported elsewhere [21].

3. Results and discussion

3.1. Combustion front velocity and temperature

Fig. 1 illustrates a typical SHS sequence recorded from the Si-adopted sample of Reaction (1) with x = 2.0. It is evident that combustion proceeds in a self-sustaining manner and features a distinct combustion wave made up of several glowing spots propagating spirally along the sample. According to Ivleva and Merzhanov [25], once the heat flux liberated from self-sustaining combustion is no longer sufficient to maintain a planar front traveling steadily, the combustion front often forms one or several localized reaction zones traversing in a spinning fashion. Because the metallothermic reactions of Nb₂O₅ and B₂O₃ with Al and Si are highly exothermic, the appearance of spinning combustion zones rather than a planar reaction front could be attributed to the endothermic mullitization process. As reported by Zaki [17], mullite (3Al₂O₃ · 2SiO₂) formation between alumina and silica absorbs energy of 67.6 kJ.

For the Si-adopted samples of Reactions (1) and (2), as presented in Fig. 2, their resulting combustion front propagation velocity decreases slightly as the Si content exceeds the stoichiometric amount. Excess Si was to compensate for the evaporation loss of Si and enhanced the silicothermic reduction

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