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Combustion Synthesis of Mullite/Metal Boride Composites

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Abstract

Formation of composite materials composed of mullite ($3Al_2O_3{\cdot}2SiO_2$) and transition metal borides (NbB_2 and TaB_2) was studied by self-propagating high-temperature synthesis (SHS). Starting materials included not only metal oxides (Nb_2O_5 and Ta_2O_5) and boron oxide (B_2O_3) as the sources of metallic elements and boron, but also Al and Si powders as the reducing agents. The evolution of mullite from in situ formed SiO_2 and Al_2O_3 and synthesis of NbB_2 and TaB_2 were investigated. The effect of excess Si addition was studied on the combustion temperature, flame-front propagation velocity, and phase composition of the final product. For formation of the NbB_2/mullite composites, the combustion velocity about 2.5 mm/s and reaction temperature around 1500 ^oC decreased slightly as the Si content increased. However, a considerable decrease in combustion front velocity from 2.74 to 1.43 mm/s and in reaction temperature from 1600 to 1250 ^oC was observed for the production of the TaB_2/mullite composites. The XRD patterns of the final products confirmed the role of excess Si in the improvement of silicothermic reduction of B_2O_3 and subsequent evolution of NbB_2, TaB_2, and mullite. The EDS analysis indicated an atomic proportion close to that of $3Al_2O_3{\cdot}2SiO_2$ for the mullite grains synthesized in this study.

Keywords: combustion synthesis, mullite, transition metal borides, XRD, SEM

1. Introduction

Mullite composites have attracted great attention due to the broadness of their industrial applications. Mullite with stoichiometries ranging from relatively silica-rich $3Al_2O_3{\cdot}2SiO_2$ (3:2 mullite) to alumina-rich $2Al_2O_3{\cdot}SiO_2$ (2:1 mullite) is the only stable crystalline phase in the aluminosilicate system [1]. For further improved fracture toughness, flexural strength, and thermal shock resistance, mullite-based composites containing ZrO_2 and Al_2O_3 were extensively studied [2-3]. Lately, other ceramic additives such as TiC and TiB_2 have gained increasing attention [4-5]. A variety of processing techniques with different starting materials have been employed to prepare mullite in either monolithic or composite forms, and they include the sol-gel method, reaction sintering, spark plasma sintering, solution combustion synthesis, self-propagating high-temperature synthesis (SHS), and thermal explosion. The SHS method takes advantage of highly exothermic reactions, and has the merits of low energy requirement, short processing time, simplicity, high productivity, and structural and functional diversity of final products [6-7]. In addition to the yield of Al_2O_3, high exothermicity of the thermite reaction is a great benefit for the SHS process. Therefore, the thermite-based SHS technique has been utilized to prepare mullite combined with ceramic or intermetallic phases.

This study aims to fabricate NbB_2/mullite and TaB_2/ mullite composites by combustion synthesis in the SHS mode. The SHS process involves coreduction of metal oxides (Nb_2O_5 and Ta_2O_5) and B_2O_3 by Al and Si. Due to the evaporation loss of Si at elevated temperatures, the effect of excess Si addition was studied on the combustion temperature, flame-front velocity and phase composition.

2. Method

The starting materials of this study include Nb_2O_5 (Strem Chemicals, < 45 μm, 99.9%), Ta_2O_5 (Alfa Aesar, < 45 μm, 99.85%), B_2O_3 (Strem Chemicals, 99.9%), Al (Showa Chemical Co., < 45 μm, 99.9%), and Si (Strem Chemicals, < 45 μm, 99%). The reactant mixtures were formulated as $13/11Nb_2O_5$ (or Ta_2O_5) + $26/11B_2O_3$ + 6Al + $(2x)$Si with $x = 1.0–2.0$ for studying the effect of excess Si ($x > 1.0$) addition.

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Sample compacts were prepared in a cylindrical shape with 7 mm in diameter, 12 mm in length, and 50% in relative density by compressing the well-mixed reactant powders. Combustion experiments were performed under high-purity (99.99%) argon of 0.15 MPa. The combustion propagation rate and reaction temperature were precisely measured. Details of the experimental setup and technique were reported elsewhere [8].

3. Results and Discussion

A typical combustion sequence illustrated in Fig. 1 is associated with formation of TaB_2/mullite from a powder compact with x = 1.0. It is evident that upon ignition the combustion front was readily formed and propagated progressively along the sample, confirming sufficiency of the reaction exothermicity.

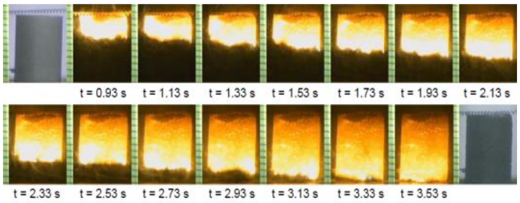


Fig. 1 A sequence of self-sustaining combustion wave

For the formation of the NbB_2/mullite composite, the combustion velocity of about 2.5 mm/s and reaction temperature of around 1500 °C decreased slightly as the Si content exceeded the stoichiometric amount. This implies a reduction in the reaction exothermicity, because the endothermic mullitization process is enhanced. However, a considerable decrease in combustion front velocity from 2.74 to 1.43 mm/s and in reaction temperature from 1600 to 1250 °C was observed for the production of the TaB_2/ mullite composites. This was attributed to the yield of $TaSi_2$ a lower exothermic phase in comparison to TaB_2. In contrast, no silicide phases existed in the NbB_2/mullite composite.

Besides mullite, niobium borides of three phases, NbB, Nb_3B_4, and NbB_2, were identified in the final product. The presence of NbB and Nb_3B_4 as the minor phases means a deficiency of boron. This was probably caused by lack of sufficient Si to fully carry out metallothermic reduction of B_2O_3. For the reactant compact with excess Si of x = 2.0, both NbB and Nb_3B_4 are considerably reduced.

The XRD pattern of the product synthesized from an exactly stoichiometric sample is shown in Fig. 2(a). First of all, the evolution of mullite from in situ formed SiO_2 and Al_2O_3 was achieved and TaB_2 was identified as the dominant boride phase, confirming coreduction of Ta_2O_5 and B_2O_3 by both Al and Si. However, the presence of free Al_2O_3 means that the evaporation loss of Si brings about a shortage of SiO_2. The lack of Si correspondingly caused incomplete reduction of Ta_2O_5 and B_2O_3. For the Si-excess samples of x = 1.5 and 2.0, Fig. 2(b) and (c) show almost no free Al_2O_3 and a slight decrease in TaB for the resulting products. This implies that the degree of silicothermic reduction of B_2O_3 was enhanced. However, excess Si considerably increased the amount of $TaSi_2$, indicative of lack of boron for the formation of TaB_2.

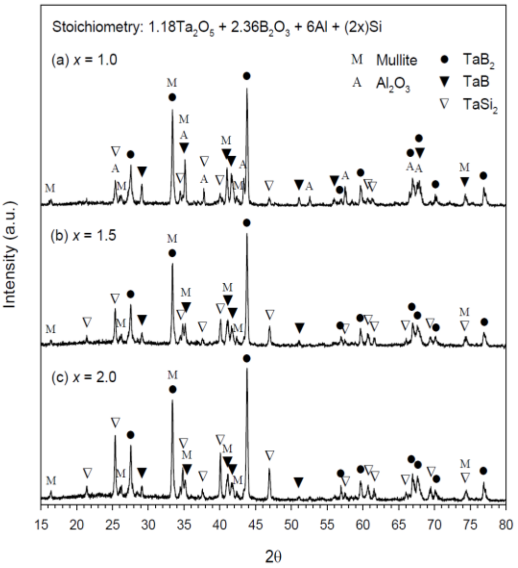
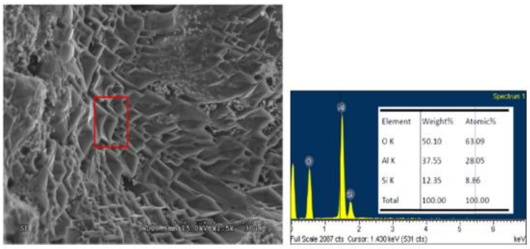


Fig. 2 XRD patterns of TaB_2/mullite synthesized from samples with Si of (a) x = 1.0, (b) x = 1.5, and (c) x = 2.0



Element	Weight%	Atomic%
O K	50.10	63.09
Al K	37.55	28.05
Si K	12.35	8.86
Total	100.00	100.00

Fig. 3 SEM micrograph and EDS spectrum of NbB_2/mullite synthesized from a sample of x = 1.5

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The typical microstructure of fracture surface of the NbB_2/mullite composite synthesized from a sample of with x = 1.5 is displayed in Fig. 3. For those plate-like grains formed into a structure with rectangular opens, the EDS analysis advises their atomic proportion of O:Al:Si = 63.09:28.05:8.86, which matches closely with that of 3:2 mullite. The other constituent NbB_2 exists as fine particles distributed over thin mullite plates.

4. Conclusions

Preparation of NbB_2/mullite and TaB_2/mullite was conducted by combustion synthesis in the SHS mode involving metallothermic reduction of Nb_2O_5, Ta_2O_5, and B_2O_3. Combustion of the sample adopting two reducing agents (Al and Si) was more exothermic and speedy than that with pre-added SiO_2 and using Al as the only reductant. It was found that the Si content about 50 mol% in excess of the stoichiometric quantity was required by the Si-containing samples to facilitate the silicothermic reduction of B_2O_3 to the utmost extent. As a result, the formation of NbB_2 or TaB_2 and mullite was improved. The mullite grains synthesized in this study showed an atomic proportion close to that of $3Al_2O_3{\cdot}2SiO_2$. In conclusion, the advantages of utilizing two reductants include more exothermic combustion, higher self-sustainability, shorter reaction time, and better phase transformation.

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