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Combustion synthesis of mullite–titanium boride composite

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Abstract

Mullite/TiB_2 composite has been prepared successfully by combustion synthesis from blends of fine TiO_2–B_2O_3–Al–SiO_2 powders. Despite the dilution effect due to silica addition and the endothermic character of mullite formation reaction, thermodynamic calculation shows that the overall reaction between the reactants is still highly exothermic. Depending on the silica grain size and the preheating temperature, partial to full conversion of reactants into products can be achieved during the process. At 550 °C preheating temperature, complete conversion of the reactants to mullite/TiB_2 was achieved. Adiabatic combustion temperature and mullite molten fraction are calculated as a function of preheating temperature.

Keywords: Mullite; Borides; Combustion synthesis

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1. Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is a typical solid solution oxide combining high melting point, low thermal expansion, good mechanical strength and resilience at elevated temperatures. Therefore, it is a potential candidate material for advanced structural applications such as kiln furniture, protection tubes, and heat insulation parts. However, monolithic mullite suffers from low fracture toughness (2.5 MPa $m^{1/2}$) and low strength (<200 MPa) [1]. A well-known processing route to improve the fracture toughness of mullite is to disperse or precipitate metastable tetragonal zirconia (t-ZrO_2) particles in a mullite matrix [2]. Addition of a carbide-reinforcing phase to an oxide matrix ceramic permits the properties of the ceramic matrix composite to be controlled in order to optimize its thermal and mechanical properties [3,4]. Addition of 20 vol.% SiC to mullite produces fracture toughness at room temperature close to 3.7 MPa $m^{1/2}$ [5]. On the other hand, hot pressed mullite matrix containing 30 vol.% TiB_2 gives a flexural strength of 427 MPa and a fracture toughness of 4.3 MPa $m^{1/2}$ [6].

Various starting materials and preparation methods are used to prepare synthetic mullite ceramics [7]. For example, a mixture of solids, a mixture of sols, or a mixture of sol and salts can each be used as the starting materials. Similarly, a variety of mullite preparation methods has been developed such as reaction sintering of mechanically mixed powders [8–13], hydrothermal treatment of mixtures of sols [14–16] and chemical vapour deposition [17–20].

Self-propagating high-temperature synthesis (SHS) is one of the rapidly emerging cost-effective technologies used to synthesize monolithic and composite in situ ceramics [21–23]. The principle of this technique is that the initial reagents, when ignited, spontaneously transform into products due to the exothermic heat of reaction. The advantages of SHS synthesis are very high-reaction rates and elimination of the need for high-temperature furnaces used in conventional material fabrication methods due to the immense energy release. The major problem to be overcome in the SHS processing of refractory ceramics is the high-retained porosity of the synthesized products. Another difficulty associated with SHS process is the very high rates of reactions which makes controlling these reactions is not a simple process [22].

Although combustion synthesis is becoming a well-known technique for synthesis of a large number of advanced materials, no previous studies, to my knowledge, has been reported about the synthesis of mullite phase in a self-sustaining manner. This may be due to the endothermic nature of the mullite formation reaction which is not classified as a self-sustaining one. On the other hand, some authors [24–26] investigated the preparation of Al_2O_3/TiB_2 composite using the highly exothermic character of the combustion reaction

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between TiO_2, B_2O_3 and Al according to the following equation:

$$TiO_2 + B_2O_3 + (10/3)Al = TiB_2 + (5/3)Al_2O_3 \quad \Delta H = -851.3\,kJ \qquad (1)$$

Conversely, the reaction between silica and alumina to form mullite is an endothermic reaction:

$$3Al_2O_3 + 2SiO_2 = 3Al_2O_3{\cdot}2SiO_2 \quad \Delta H = 67.6\,kJ \qquad (2)$$

Although reaction (2) cannot proceed alone by self-sustaining manner due to its endothermic character, the overall reaction (3) is still highly exothermic where the heat released by progress in reaction (1) can induce reaction (2) between the liberated alumina and the added silica.

$$TiO_2 + B_2O_3 + (10/3)Al + (10/9)SiO_2 = TiB_2 + (5/9)(3Al_2O_3{\cdot}2SiO_2) \quad \Delta H = -813.8\,kJ \qquad (3)$$

Therefore, this work is aimed to maximize the benefit of the heat released from the exothermic reaction between TiO_2, B_2O_3 and Al through generating an endothermic reaction between the liberated alumina and silica to form mullite in a self-sustaining manner. The effect of silica grain size, preheating temperature and silica stoichiometry on the degree of completion of mullite phase formation is investigated.

2. Experimental procedure

The materials used in this study were titanium dioxide of 98% purity and <1 μm particle size (Nice Chemical Pvt. Ltd., India), aluminum metal powder of 99.5% purity and <36 μm particle size (GFS Chemicals Inc., USA), boron oxide B_2O_3 of 97% purity and less than 32 μm grain size (Fluka, USA) and silica 99% purity having different grain sizes from <71 to <20 μm (Riedel-de Haen, Germany). The powders were mixed in the required molar ratio to form $3Al_2O_3{\cdot}2SiO_2/TiB_2$ composite and dry blended in a slow rotating mill with alumina ball for 5 h. The powder mixture was uniaxially pressed without binder at 78 MPa into cylindrical compact of 2.0 cm height and 1 cm diameter to approximately 55% relative density. The compact was transferred to combustion reactor and placed on a movable graphite plate. The reactor was evacuated and backfilled with pure argon at 1 atm. The initial temperature of the green compact was increased using a resistance coil and was kept constant for 15 min before ignition. The ignition was carried out using an electric spark above the compacts in open atmosphere. The electricity was supplied from an ac power source (30–40 A). The combustion temperatures were recorded using thermocouple of type C (tungsten 5% rhenium–tungsten 26% rhenium, Nilaco Corporation, Japan) of 0.2 mm thickness with bead size of approximately 0.4 mm. Data acquisition board (NI-DAQ 6023 E series, National Instruments Co., USA) was used to acquire the output mV from the W–Re thermocouple using a separate channel and configured to collect data at a rate of a sample each 15 ms. Detailed procedure of carrying out combustion reaction was previously published [27]. Different phases of the combustion products were identified by X-ray diffraction analysis using X-ray diffractometer (D8 Advanced Bruker AXS, GMbH, Karlsruhe, Germany). This instrument and its accompanied software were also used to perform semi-quantitative analysis of different product phases. Microstructure of specimens was investigated using scanning electron microscope (SEM, Model JSM-5410, JEOL, Tokyo, Japan) equipped with electron dispersive spectroscopy (EDS). SEM investigation is conducted on polished sections coated with gold to ensure good electrical conductivity of the entire components of the sample.

3. Results and discussion

3.1. Thermodynamic calculations

The adiabatic combustion temperature of reaction (3) as well as the molten fraction of mullite phase can be calculated at any initial temperature T_0 from the following equation:

$$-\Delta H_{r,298} + \int_{298}^{T_0} C_p\left(TiO_2 + B_2O_3 + \tfrac{10}{3}Al + \tfrac{10}{9}SiO_2\right) dT = \int_{298}^{T_{ad}} C_p(TiB_2)_s\, dT \times \frac{5}{9}\int_{298}^{2123} C_p(3Al_2O_3\cdot 2SiO_2)_s\, dT + \frac{5}{9}\int_{2123}^{T_{ad}} C_p(3Al_2O_3\cdot 2SiO_2)_l\, dT + \tfrac{5}{9}\gamma\, \Delta H_{f,3Al_2O_3\cdot 2SiO_2} \qquad (4)$$

where $\Delta H_{r,298}$ is the enthalpy change of reaction (3), C_p is the specific heat capacity [28], γ is the fraction of molten mullite and $\Delta H_{f,3Al_2O_3\cdot 2SiO_2}$ is the enthalpy of fusion of mullite and equals to 319.9 kJ/mol [29].

Fig. 1 shows the adiabatic combustion temperatures calculated from Eq. (4) as a function of preheating temperature for the combustion synthesis of mullite/TiB_2 composite according to reaction (3). The adiabatic combustion temperature at 25 °C has a value of 1850 °C which equals the melting point of mullite and higher than that of silica. The calculation shows that about 57.1 wt.% of mullite is in a molten state. This means that a portion of heat released from reaction (3) (712.3 kJ) is used to heat up the combustion products to

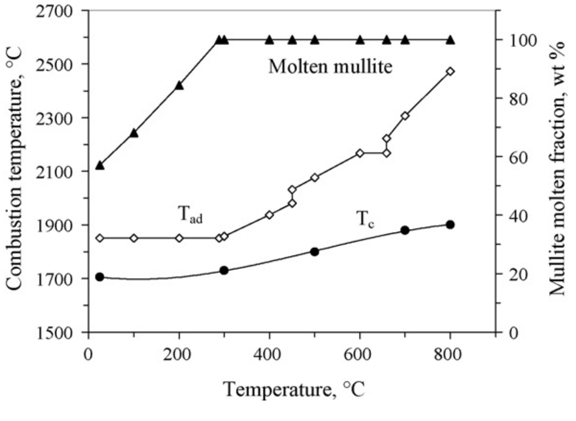

Fig. 1. Dependence of adiabatic and measured combustion temperatures (T_{ad} and T_c) and molten fraction of mullite on the preheating temperature.

1850 °C while the remaining amount (101.5 kJ) is consumed in melting 57.1 wt.% of mullite. The value of adiabatic temperature does not increase beyond 1850 °C by further increase in the initial temperature up to 289 °C and still constant due to the transformation of additional amounts of mullite phase into molten state (Fig. 1). The quantity of energy required to melt the remaining amount of mullite (42.9 wt.%) equals to 76.2 kJ. The calculation shows that this amount of energy can be offered by preheating the reactant to 289 °C before the ignition. Therefore, at 289 °C the total amount of system energy (890 kJ) is enough to raise the temperature of the product to 1850 °C and melts the entire quantity of mullite. Beyond 289 °C, the adiabatic temperature of the product starts to increase linearly due to the step-wise accumulation of energy provided by further increasing the preheating temperatures.

3.2. *Effect of silica grain size*

A variety of silica powders having different grain sizes (<71, <36 and <20 μm) is used to investigate the effect of silica grain size on the degree of mullite phase formation. The particle sizes of the other reactants are kept constant, while one stoichiometry of silica is used in this series of experiments. Despite the dilution effect of silica (21.7 wt.%) and the variety of its grain size, the compacts are successfully ignited at room temperature with a combustion temperature of 1705 °C in case of <20 μm sample. XRD patterns of the different combustion products, Fig. 2, show the formation of TiB_2, Al_2O_3 and mullite as dominant phases while very little amount of residual SiO_2 is noticed only in case of <36 and <71 μm grain size silica. Semi-quantitative analysis of different phases of products is given in Table 1. As the silica grain size is reduced, the degree of mullite formation increases with a simultaneous decrease in the amounts of alumina and residual silica. At silica particle size of <20 μm no residual silica appears in the XRD analysis and at the same time low intensity alumina peaks still exist. It is clear that there is a strong dependence of the mullite formation on the silica particle size. This is an expected behavior because decreasing silica grain sizes leads to a more homogenous distribution of silica grains in the reaction media and the contact area between the liberated alumina and silica particles should increase too. Although one stoichiometry value of silica is used, considerable amount of alumina still exists in the reaction product along with the disappearance of silica as indicated by XRD analysis. The incomplete mullitization of alumina may be because either the amount of energy liberated by igniting the compact at room temperature is not enough and consequently additional heat should be given to the reactant before ignition or one stoichiometry value of silica is not sufficient.

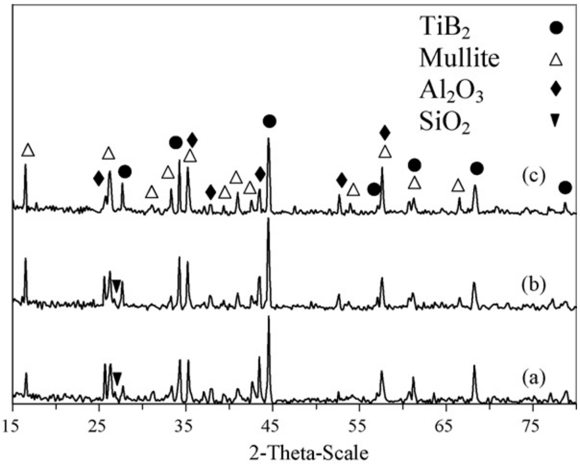

Fig. 2. XRD of combustion products synthesized without preheating using different silica grain sizes: (a) <71 μm, (b) <36 μm, and (c) <20 μm.

Table 1
Semi-quantitative analysis of combustion product synthesized using different silica grain sizes

Silica grain size (μm)	Product composition (wt.%)			
	TiB_2	Al_2O_3	Mullite	SiO_2
<71	23	50	22	5
<36	22	43	33	2
<20	20	30	50	–

3.3. *Effect of preheating*

A useful parameter that can be used in order to boost the self-sustaining formation of mullite is achieved by preheating the reactants prior to the ignition. Preheating the reactant is usually used to induce the less exothermic reactions to proceed in a self-propagating style where higher adiabatic temperatures and reaction rates are attained [27].

Fig. 1 represents the measured combustion temperature as a function of preheating one. XRD patterns corresponding to the combustion products preheated at different temperatures up to 700 °C are given in Fig. 3. It is found that, the mullite formation is very sensitive to the preheating temperature. The peaks'

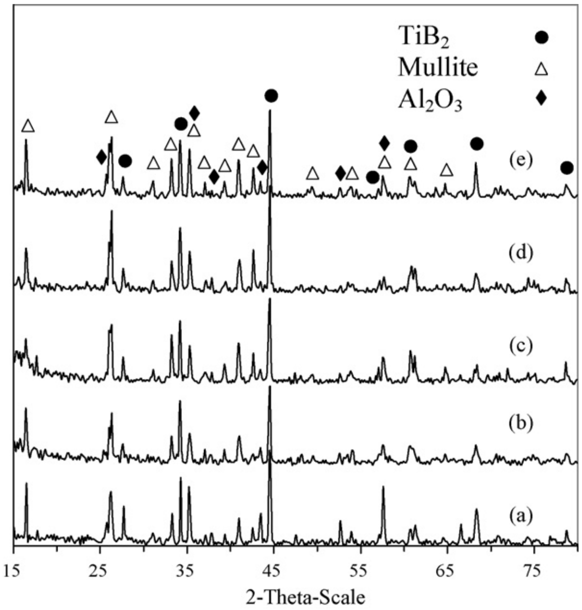

Fig. 3. XRD of combustion products synthesized using one silica stoichiometry at different preheating temperatures: (a) without preheating, (b) 300 °C, (c) 500 °C, (d) 550 °C and (e) 700 °C.

Table 2
Semi-quantitative analysis of combustion products synthesized at different preheating temperatures and different stoichiometric values of silica

Preheating temperature (°C)	1.0 stoichiometry silica			1.25 stoichiometry silica		
	TiB_2	Al_2O_3	Mullite	TiB_2	Al_2O_3	Mullite
25	20	30	50	22	21	57
300	21	21	58	23	11	66
500	23	13	64	22	4	74
550	23	8	69	21	–	79
700	22	10	68	21	6	73
800	21	15	64	20	13	67

intensity corresponding to alumina continuously decreases with increasing the preheating temperature and it reaches a minimum at 550 °C. Beyond 550 °C, the alumina diffraction pattern intensity increases once again with further preheating. The semi-quantitative analysis shows the same trend (Table 2). These results indicate that at lower preheating temperatures some amounts of silica are remaining in the products in amorphous state and that raising the initial temperature speeds up the reaction between silica and alumina. In addition, these results also demonstrate that one stoichiometry value of silica is not sufficient to attain complete reaction with the liberated alumina and that increasing amount of silica may be necessary.

Therefore, samples having 1.25 stoichiometry of silica are prepared and ignited at the same initial temperature range. Despite the increasing amount of silica (25.8 wt.% of the charge), the compact is easily ignited at room temperature. XRD, Fig. 4, shows the same trend as in case of one stoichiometry sample. However, at 550 °C the alumina pattern is completely disappeared which indicates a complete reaction

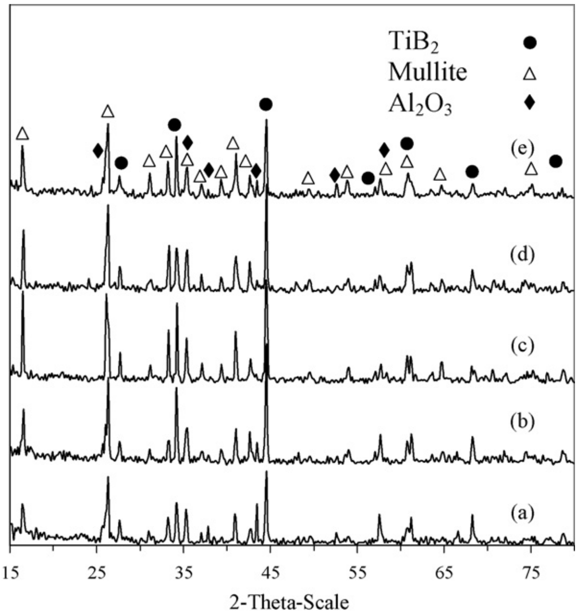

Fig. 4. XRD of combustion products synthesized using 1.25x silica stoichiometry at different preheating temperatures: (a) without preheating, (b) 300 °C, (c) 550 °C, (d) 700 °C and (e) 800 °C.

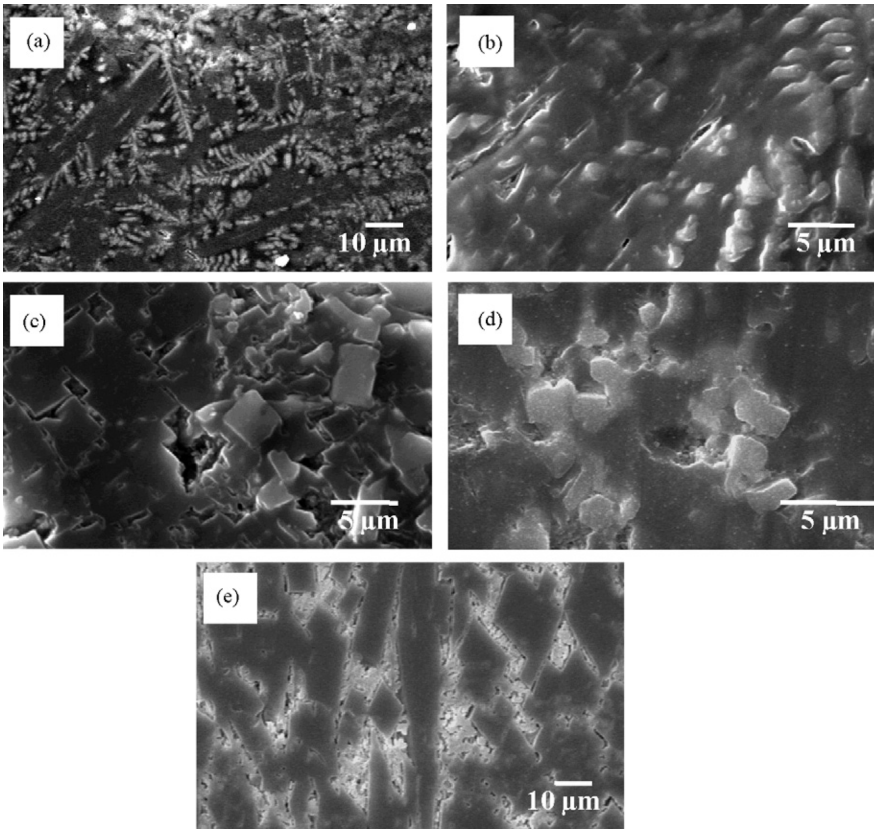

Fig. 5. SEM images of the combustion products of TiO_2–B_2O_3–(10/3)Al synthesized using: (a) 1x silica without preheating, (b) 1.25x SiO_2 without preheating, (c) 1.25x SiO_2 300 °C, (d) 1.25x SiO_2 550 °C and (f) 1.25x SiO_2 800 °C.

between the liberated alumina and 1.25 stoichiometry silica. Again above 550 °C, alumina phase is observed. The reappearance of alumina can be attributed to the thermal decomposition of limited quantities of mullite phase into alumina and silicon monoxide due to the very high combustion temperature according to the reaction:

$$3Al_2O_3\cdot 2SiO_2 = 3Al_2O_3 + 2SiO + O_2 \quad (5)$$

Unlike alumina, which is thermodynamically stable at very high temperatures, mullite can thermally decompose at elevated temperatures with the evolution of silicon monoxide [30,31]. Park and Mcnallan [4] reported that monolithic mullite is stable at temperatures below 2027 °C and at higher temperatures it breaks down leading to production of alumina and SiO. This decomposition temperature is dramatically lowered to 1227 °C in the presence of 10% SiC.

3.4. Microstructure

Fig. 5 shows the effect of preheating temperature on the microstructure of the combustion products. Generally, mullite forms dark grey continuous phase where both residual alumina grains (light grey) and very small titanium boride grains (bright hexagonal grains) are disseminated in the mullite matrix. In case of 1.0 and 1.25 stoichiometry of silica (without preheating), residual alumina is separated in a dendritic form which is predominated in case of 1.0 stoichiometry sample (Fig. 5a and b). At 300 °C preheating temperature, Fig. 5c, small rhombohedral alumina grains and some of its relict grains are identified. Raising the preheating temperature increases the percentage of mullite phase and decreases the amount of residual alumina till it vanishes completely at 550 °C (Fig. 5d). Prismatic mullite grains are clearly observed at 800 °C. It is worthy to mention that all the combustion products are highly porous and containing many cracks which are the general phenomena characterizing the combustion reactions.

4. Conclusions

Self-propagating high-temperature synthesis has been successfully utilized to generate simultaneous endothermic and exothermic reactions where the energy required for the endothermic reaction is offered by the heat evolved from the exothermic one. Mullite containing about 22 wt.% TiB_2 with different varieties of alumina percentage ranging from about 0 to 30 wt.% has been prepared in a self-sustaining manner by the reaction between added silica and the alumina liberated from the exothermic reaction of $TiO_2/B_2O_3/Al$ mixture. Mullite formation is favored by decreasing silica grain size and increasing preheating temperature up to 550 °C. Mullite phase is found to be thermally decomposed upon increasing the preheating temperature over 550 °C.

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