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Journal of the European Ceramic Society 29 (2009) 1485–1492
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Effects of additives on combustion synthesis of Al_2O_3–TiB_2 ceramic composite

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Received 30 June 2008; received in revised form 29 August 2008; accepted 11 September 2008
Available online 19 October 2008

Abstract

Al_2O_3, SiC and kaolin were employed as additives in combustion synthesizing Al_2O_3–TiB_2 ceramic composite. Effects of the additives on adiabatic temperature, combustion wave velocity, volume change and composite density were studied, and bending strength of the synthesized ceramics was evaluated. By theoretical calculation, the adiabatic temperature of Al–TiO_2–H_3BO_3 system is 2314.85 °C and decreases with increasing the additive addition. With Al_2O_3 addition, the phases presented in the ceramic composite are unchanged, and the phases of SiC and $3Al_2O_3{\cdot}2SiO_2$ emerges when SiC and kaolin are added. The addition of the additives results in a refined TiB_2 particulate size and reduces combustion wave velocity. The highest density is achieved with the addition of kaolin from 10 to 30 wt.% making the volume change from −4.6 to −1.2%. The bending strength of the TiB_2–Al_2O_3 composite is improved eight times with the addition of 30 wt.% kaolin.

Keywords: Refractories; Strength; Composites; Combustion synthesis; Sintering

1. Introduction

TiB_2 particulate is particularly attractive owing to its extreme hardness, superior wear resistance, high melting point, good thermal stability, and high strength at elevated temperatures. An effective way to produce TiB_2-containing metal and ceramic matrix composites is self-propagation high temperature synthesis (SHS)[1–3] without the requirement of high temperature furnace and long processing time. The materials prepared by SHS methods have advantages including high purity of the reaction products, low energy consumption and low cost.[2,4]

During the synthesis of Al_2O_3–TiB_2 ceramic composite, the precursor powders of the self-propagation high temperature synthesis were Al, TiO_2[5] and B or B_2O_3,[6] and the combustion reactions proceed according to the following reactions:

$$4Al + 3TiO_2 + 6B \rightarrow 2Al_2O_3 + 3TiB_2 \quad (1)$$

$$10Al + 3TiO_2 + 3B_2O_3 \rightarrow 5Al_2O_3 + 3TiB_2 \quad (2)$$

Stoichiometrically, the variation between reactions (1) and (2) is the difference in TiB_2 contents of the reaction products.

Due to the high melting point and high vapor pressure of the constituents,[7,8] the Al_2O_3–TiB_2 ceramic composite prepared by reactions (1) and (2) through the SHS route is porous, and a densification process is necessary to obtain dense materials.[9] However, the consolidation of the material into dense and high-strength is difficult because of the high degree of covalent bonding and low self-diffusion coefficient of the constituent elements. Relatively high densities are achieved only by pressure-assisted sintering procedures at temperatures higher than 1900 °C, i.e. temperatures exceeding 70% of the absolute melting temperature.[10,11] The introduction of sintering aids such as Fe, Ni, Co, W, C and WC improves the final density and allows a lower densification temperature with increased volume diffusion and retarding evaporation mechanisms.[12]

From an economical consideration, the use of B_2O_3 in place of element B in reaction (1) creates a significant cost saving, as the cost of B_2O_3 is less than 1% of that of boron. However, the substitution of B_2O_3 by H_3BO_3 in reaction (2) is technologically more attractive in synthesizing Al_2O_3–TiB_2 ceramic composite.

Boric acid (H_3BO_3) can be regarded as a hydrate of boron oxide and is formulated as $B_2O_3{\cdot}3H_2O$ or $B(OH)_3$ for orthoboric

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doi:10.1016/j.jeurceramsoc.2008.09.005

acid, and $B_2O_3{\cdot}H_2O$ or HBO_2 for metaboric acid; boron oxide (B_2O_3) is obtained as a final product when orthoboric acid is heated.[13] Orthoboric acid (H_3BO_3) transforms into metaboric acid (HBO_2) above 100 °C by losing a water molecule, and a viscous fluid mixture consisting of HBO_2 and B_2O_3 is obtained around 170 °C at normal atmosphere. Ortho- and metaboric acids have a high volatility between 104 and 200 °C. Orthoboric acid is white, triclinic crystals with a melting point of 171 °C and density of 1.52 g/cm^3.[14]

With H_3BO_3 as a precursor powder, reaction (2) becomes:

$$10Al + 3TiO_2 + 6H_3BO_3 \rightarrow 5Al_2O_3 + 3TiB_2 + 9H_2O \quad (3)$$

The Al_2O_3–TiB_2 composite resulting from reaction (3) will be more porous due to the vaporization of the water from decomposition of the H_3BO_3 which also has an additional mass lost on ignition.[15]

The previous experimental results of the current author showed that the strength of the sintered body by the reactants in reaction (3) was very low without pressure assistance during the synthesis process. To improve the strength of the sintered body, the vigorous release of vapor from boric acid decomposition has to be retarded at a depressed combustion temperature under the combustion synthesizing condition. This paper reports the initial efforts to prepare the Al_2O_3–TiB_2 composite by SHS without pressure assistance, aiming at developing a cheap and simple technology to use in refractory production. The additives of Al_2O_3, SiC and kaolin were employed to attenuate the vigorousness of reaction (3) and serve as sintering aids to promote densification of the reaction products at low temperatures. Their effects on adiabatic temperature, combustion wave velocity, volume change and density of the composite were studied, and the strength of the synthesized ceramics was evaluated by bending test.

2. Experimental procedure

The reactant powders of Al, TiO_2 (rutile) and H_3BO_3 were chemically pure with the sizes <25 μm, and Al_2O_3 (>90%, −200 mesh); SiC (>95%, 14 μm) and kaolin (>95%, −1800 mesh) were used as additives.

According to reaction (3), certain amounts of an additive were added into the reactant powders so that the additive content is 10, 20 and 30 wt.% of the total sintered body, respectively.

The reactant powders were mixed with a given amount of de-ionized water and cold pressed into the green compacts of 112 mm × 21 mm × 12 mm under a constant pressure. Desiccation of the green compacts was carried out in a resistance furnace at 160 °C for 5 h. The sintering of the green compacts was carried out in air, and the ignition of the combustion reaction was done by using an electric arc generated by graphite electrodes. The movement of combustion wave front is recorded for calculating combustion wave velocity of the reaction with different additions of the additives. After completion of the combustion reaction, the sintered ceramics were cooled in air to room temperature.

The samples for metallography were cut from the sintered green compact. Microstructure observation was conducted under scanning electron microscope, and X-ray diffractometry (XRD) analysis was carried out under a D/Max-3B X-ray diffractometer using Cu Kα radiation on the sintered ceramic composite to detect the phase present at different additive additions.

Bending of the sintered composites were conducted with 40 mm span at a loading rate of 50 kN s^{-1} under a WE-10 mechanical property test machine, and 55 mm × 40 mm × 20 mm test samples were machined from sintered body of Al_2O_3–$3TiB_2$ composite with the dimensions of 60 mm × 45 mm × 25 mm.

3. Results and discussions

3.1. Adiabatic temperature of Al–B_2O_3–TiO_2 system

Thermodynamic analysis is the basis of evaluating whether a SHS reaction is self-sustainable. An empirical criterion was proposed that a synthesis reaction is self-sustainable if combustion temperature is equal to or over 1526.85 °C. Otherwise, supplemental energy needs to be provided from the external environment.[16,17] In order to attenuate thermal explosion effect, kaolin, aluminum oxide and silicon carbide are added into the green compact of the reaction powders. The decrease in adiabatic temperature of the reaction by adding the additives can be calculated according to reaction thermodynamics.

Suppose reaction (2) is conducted under adiabatic condition and completed by chemical stoichiometry. The isobaric enthalpy of an isolated system is a constant according to the first law of thermodynamics, which means that the enthalpy of reactants at room temperature T_0 is equal to the one of reaction products under adiabatic temperature T_{ad}. This is expressed as[18]:

$$\sum n_i H_{T0} = \sum m_j H_{T\mathrm{ad}} \quad (4)$$

where H presents enthalpy, n and m stand for molal quantity of reactants and products, subscript i and j denote the components of reactants and products, respectively.

Based on thermodynamic data,[19] the sum of reactant enthalpies at 24.85 °C is −6650 kJ, and the relation of reaction product enthalpies and temperature is established, as shown in Fig. 1. Linear fitting of the data in Fig. 1 obtains:

$$\sum m_j H_{T\mathrm{ad}} = -9981 + 1.268T \ \text{(kJ)} \quad (5)$$

Substituting $\Sigma m_j H_{T\mathrm{ad}}$ in Eq. (4) with Eq. (5), the adiabatic temperature T_{ad} of Reaction (2) is 2353.85 °C which is close to the maximum adiabatic temperature 2234.85 °C measured in the reaction system.[20]

Repeating the above calculation for reaction (3), the adiabatic temperature of Al–TiO_2–H_3BO_3 system is 2314.85 °C. The decrease in the adiabatic temperature by replacing B_2O_3 with H_3BO_3 in the system results from the H_3BO_3 dissolution reaction which consumes additional heat released from the reaction during the self-propagation high temperature synthesis process.

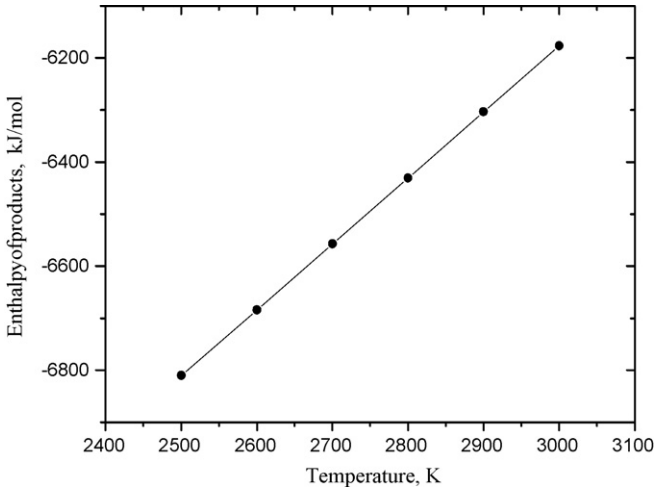

Fig. 1. Relation of enthalpy of products and temperature.

3.2. Effect of the additives on adiabatic temperature

With the introduction of an inert additive into reaction (3), the calculation formula for its adiabatic temperature becomes:

$$\sum n_i H_{T0} + \sum f_k H_{T0} = \sum m_j H_{T\mathrm{ad}} + \sum f_k H_{T\mathrm{ad}} \quad (6)$$

where f_k is molal quantity of additive.

The calculation results of the adiabatic temperature changing with the additions of Al_2O_3, kaolin and SiC are shown in Fig. 2. The adiabatic temperature of the reaction system is decreased with the increase in the additive addition. The more additives in the green compact the less heat generated by the reactants, resulting in the decreased adiabatic temperature. In contrast with the data in Table 1, it is worth noticing that a certain amount of unmelted aluminum oxide existed in all the additives with the additions covered by the horizontal line in Fig. 2, which accords with the calculations by Xia et al.[18] The existence of the same adiabatic temperature for the system with different additive additions lies in the fact that the heat release from the action is enough to raise the system temperature above the melting point of Al_2O_3, but insufficient for the complete fusion of the whole Al_2O_3 component.

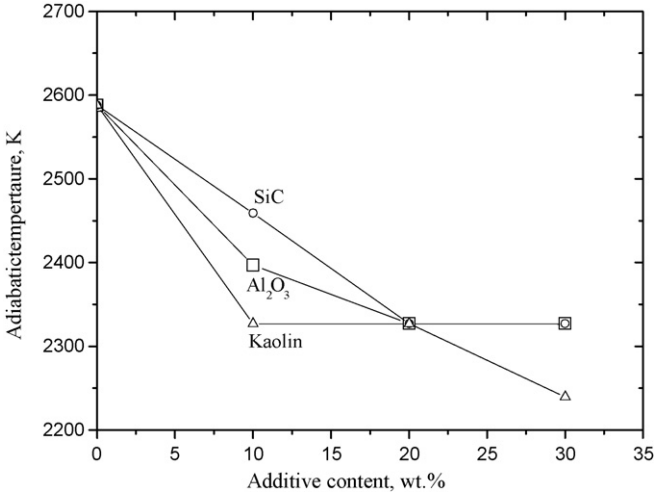

Fig. 2. Effect of different additives on adiabatic temperature.

3.3. Phase analysis

Only the phases of TiB_2 and Al_2O_3 occur in the sintered body of the reaction products without any kind of additive addition as shown in Fig. 3(a), and no unreacted reactants and intermetallics phases such as TiB and Al_3Ti are detected. However, the existence of Al–Ti and B–Ti compounds in the final product cannot be eliminated. In fact, any weighing of the reactants is unable to keep an exact reaction stoichiometry, and very minimal excess of Al would cause the precipitation of B or Ti aluminide due to their very limited solubilities in Al.[23,24]

With the addition of Al_2O_3, the phases presented in the sintered body are the same as the ones without any additive addition. More Al_2O_3 addition has no effect on phase constitutes except for the increase in Al_2O_3 peak values, as shown in Fig. 3(b). SiC addition results in the reduction of the diffraction peaks for both TiB_2 and Al_2O_3 phases, while SiC peaks become greater with increasing SiC addition, as shown in Fig. 3(c). Apart from the TiB_2 and Al_2O_3 phases, a $3Al_2O_3{\cdot}2SiO_2$ phase occurs also when kaolin is added in the system, as shown in Fig. 3(d). During the combustion reaction, the kaolin decomposes according to Ref. [25] by

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \xrightarrow{600\,^{\circ}C} Al_2O_3 \cdot 2SiO_2 + 2H_2O \quad (7)$$

and

$$3(Al_2O_3 \cdot 2SiO_2) \xrightarrow{960\,^{\circ}C} 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 \quad (8)$$

Since no SiO_2 phase is detected in the reaction products, it should have reacted with Al_2O_3 and formed $3Al_2O_3{\cdot}2SiO_2$ during the SHS process.

3.4. Microstructures of the synthesized green compacts

The typical microstructure of the sintered Al–TiO_2–B_2O_3–H_3BO_3 powder compact without any additive addition is shown in Fig. 4 in which TiB_2 particles ranging from 1.3 to 2.5 μm are dispersed in aluminum oxide matrix. The morphology of the TiB_2 particle is mostly short claviform due to its C32 crystal structure of hexagonal system,[26] although other shapes of TiB_2 particle were formed under different processing parameters.[27] The cavities in the aluminum oxide matrix should be the result of gas release from H_3BO_3 dissolution at high temperature.

With 20 wt.% Al_2O_3 addition, the corresponding microstructure of the sintered body is shown in Fig. 5(a) where the small particles are TiB_2, and the big ones are partially melted Al_2O_3 with unmelted cores. In contrast with Fig. 4, the size of the TiB_2 particles is greatly reduced, and the shape becomes blocky. The same amount of SiC and kaolin additions results also in a smaller size of TiB_2 particles. This is shown in Fig. 5(b) and (c) in which the TiB_2 particles are indistin-

Table 1
Liquid phase of Al_2O_3 in reaction products at adiabatic temperatures.

Additive	Melting point (°C)	Amount (wt.%)	Adiabatic temperature (°C)	Liquid Al_2O_3 (%)
–	–	0	2314.85	100
Al_2O_3	2053.85	10	2123.85	100
		20	2053.85	64.5
		30	2053.85	18.3
SiC	2829.85[21]	10	2183.85	100
		20	2053.85	87.9
		30	2053.85	31.0
Kaolin	1749.85[22]	10	2053.85	98.7
		20	2053.85	86.0
		30	2000.85	0

guishable from the Al_2O_3 particles partially melted at the combustion reaction temperatures. In the case of kaolin addition, the $3Al_2O_3{\cdot}2SiO_2$ phase detected by X-ray diffraction is commingled with aluminum oxide and unable to determine its existence morphologically. The size refinement of the TiB_2 particles comes mainly from the increased preferential nucleation of the particles on the additive surface with less nucleation energy. The unmelted Al_2O_3 should have a great impeding effect on TiB_2 nuclear growth except for its step-like surface which favors crystal nucleation.[25] The reason of the particle shape change is owing to the reduced combustion temperatures, resulting in the difficulty and time shortage of TiB_2 self-diffusion from the corner part into its body at high temperature.

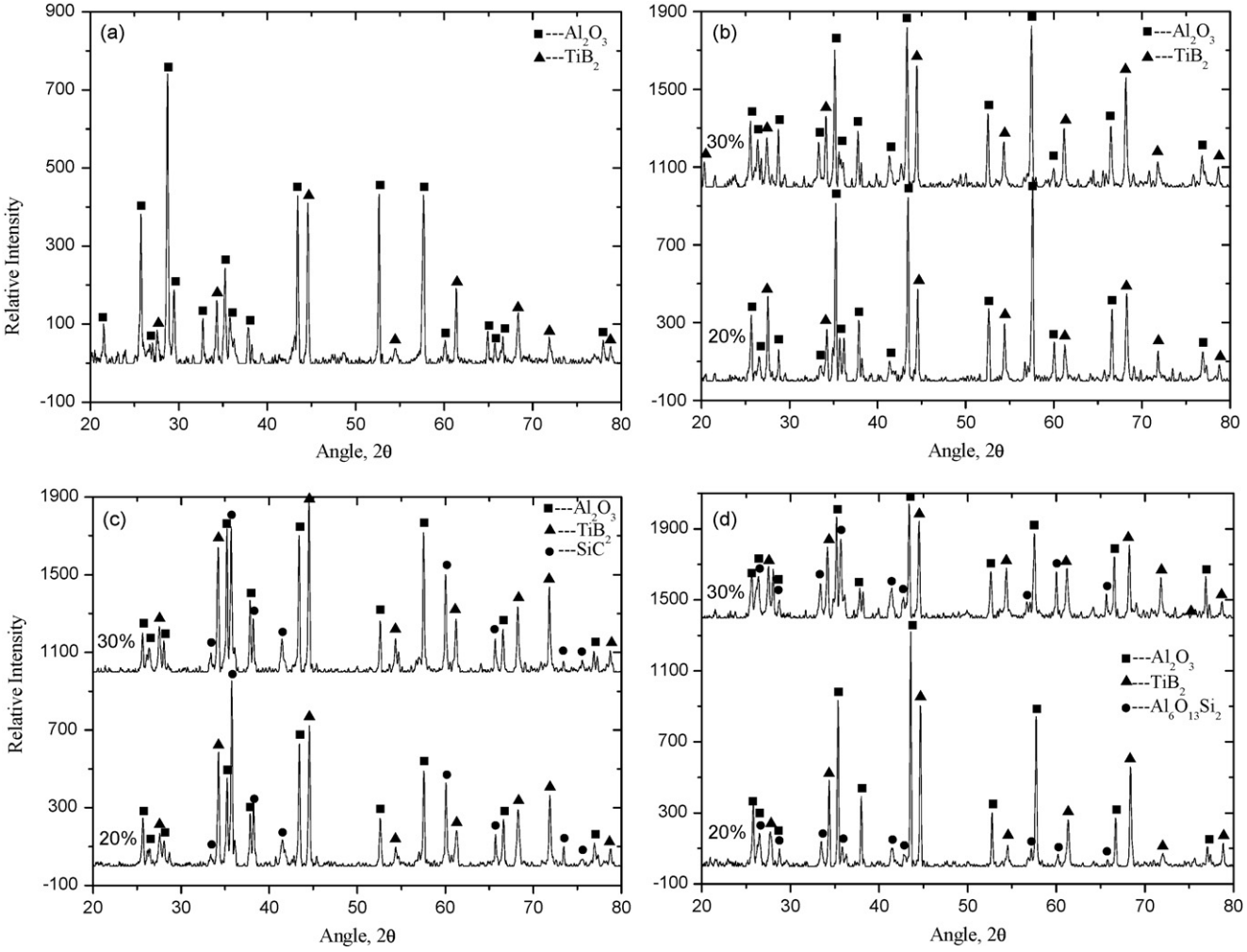

Fig. 3. Phase analysis of the Al_2O_3–TiB_2 composite (a) without additive additions and with the addition of (b) Al_2O_3, (c) SiC and (d) kaolin.

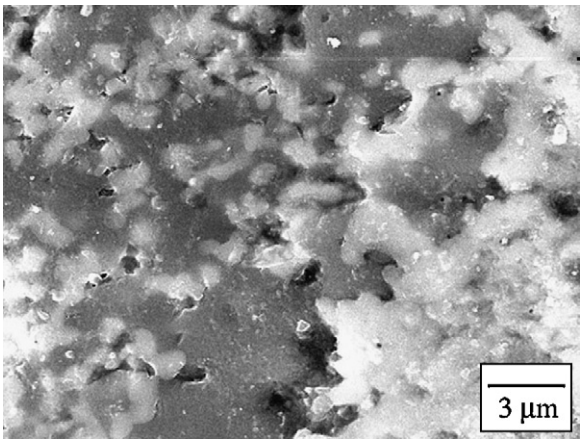

Fig. 4. Microstructure of sintered Al–TiO_2–B_2O_3–H_3BO_3 powder compact.

3.5. Combustion wave velocity

In a combustion reaction system, if the heat loss by convection and radiation is negligible, the propagation velocity of combustion wave, V is determined by[28]

$$V^2 = f(n)\frac{C_p k}{q}\frac{RT_c^2}{E}K_0 \exp\left(\frac{-E}{RT_c}\right) \quad (9)$$

where $f(n)$ is a dynamic function of nth-order reaction, q and E are heat generation and activation energy of the reaction, C_p stands for heat capacity of reaction products, T_c is combustion temperature, R and k present gas and Boltzmann constants respectively, and K_0 is a constant. Apart from the characters of reactive materials and reaction products, the factors influencing combustion velocity are related to stoichiometric proportion, green density and additive addition.

The combustion wave velocity of the green compact without any additive addition to the Al–TiO_2–H_3BO_3 system is 5.5 mm/s, as shown in Fig. 6. When Al_2O_3, SiC and kaolin are added, respectively, the combustion wave velocity is rapidly decreased with increasing the additive additions. With the same quantity of addition, the fastest combustion velocity happens in adding SiC, and the lowest one occurs in kaolin addition, which may be concerned with the heat conductivities of the additives. With increasing additive content, the quantity of the reactants is decreased, resulting in less heat generated by the reaction; consequently, the adiabatic temperature declines. As chemical reaction rate is proportional to temperature, the decrease in adiabatic temperature brings the inevitable drop in combustion temperature.

3.6. Volume change of the TiB_2–Al_2O_3 composite

The specimens synthesized with different additive additions are shown in Fig. 7. Obviously, the additives and additions have a significant impact on the dimension changes of their green compacts with the same sizes.

As seen in Fig. 8, the volume of the TiB_2–Al_2O_3 composite is increased with the increase in the addition of all the additives. The additions of the Al_2O_3 and SiC produce positive volume changes, which mean the volumes of the sintered body are greater than those of the green compacts. With 30 wt.% Al_2O_3 and SiC additions, the expansions of the resulted composites are about 7% of their initial volume. However, the addition of kaolin in the reactant powders creates volume contraction of the sintered TiB_2–Al_2O_3 composite. With the increase in kaolin content from 10 to 30 wt.%, the volume of the sintered body changes from −4.6 to −1.2% in contrast with the volume of the green compact This indicates a possible way of approximate shape processing TiB_2–Al_2O_3 ceramic articles by self-propagation high temperature synthesis of Al–TiO_2–H_3BO_3 powders with proper addition of kaolin.

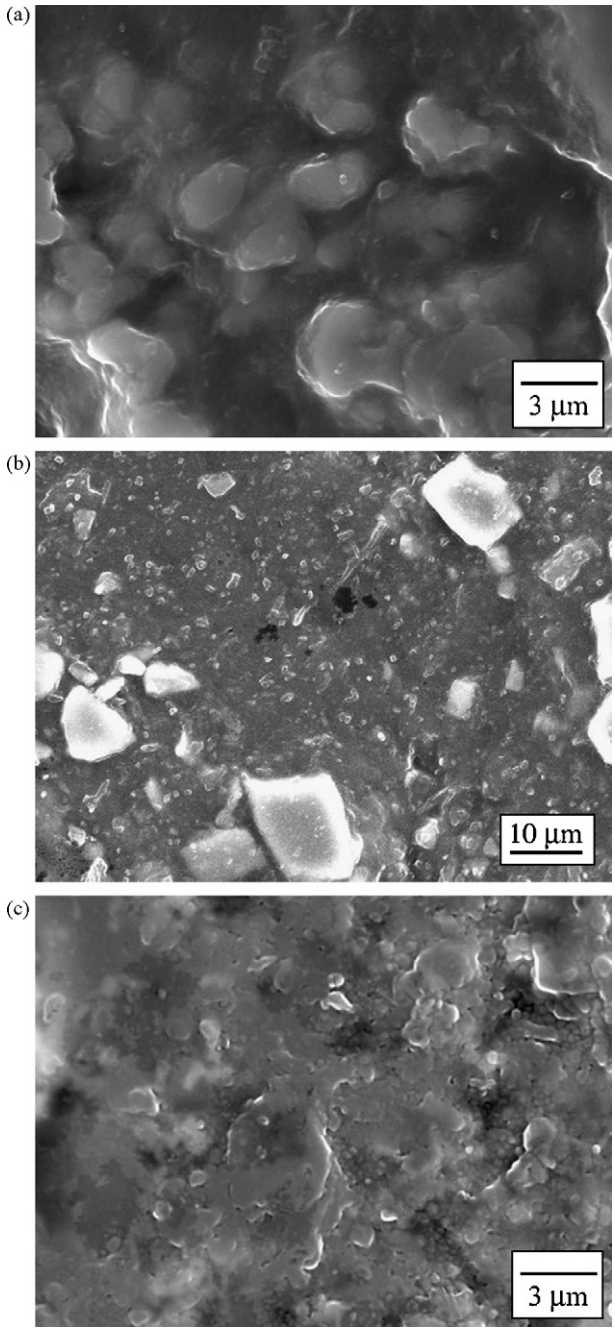

Fig. 5. Microstructure of sintered Al–TiO_2–B_2O_3–H_3BO_3 green compacts with 20 wt.% additions of (a) Al_2O_3, (b) SiC and (c) kaolin.

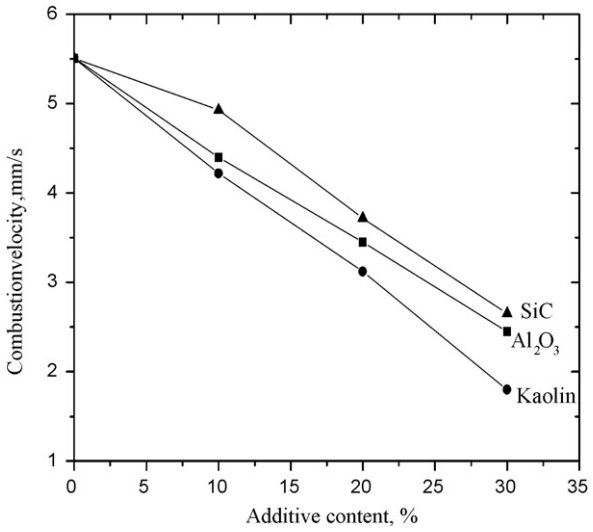

Fig. 6. Effect of the additives on combustion velocity of the Al–TiO_2–H_3BO_3 green compacts.

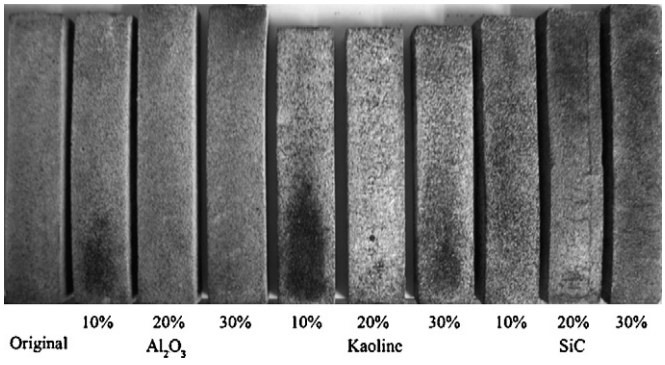

Fig. 7. SHS specimens with different additive additions.

3.7. Densities of the TiB_2–Al_2O_3 composite with different additives

Fig. 9 shows the densities of the TiB_2/Al_2O_3 composite with different additive species and quantities. Obviously, the densities of all the composites are far below their theoretical densities as listed in Table 2. The lowest density of the TiB_2–Al_2O_3 composite without additive addition lies in the cavities formed by (a) more consumption of fugitive constituents at the relatively high combustion temperature by the strenuous reaction; (b) poor wettability between Al_2O_3 and TiB_2[29]; and (c) higher volume of vapor released by H_3BO_3 dissolution.

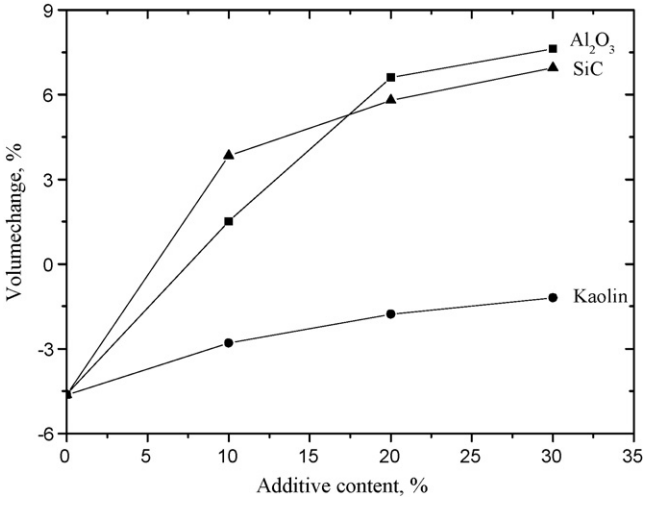

Fig. 8. Effect of additives on volume change of the TiB_2–Al_2O_3 composite.

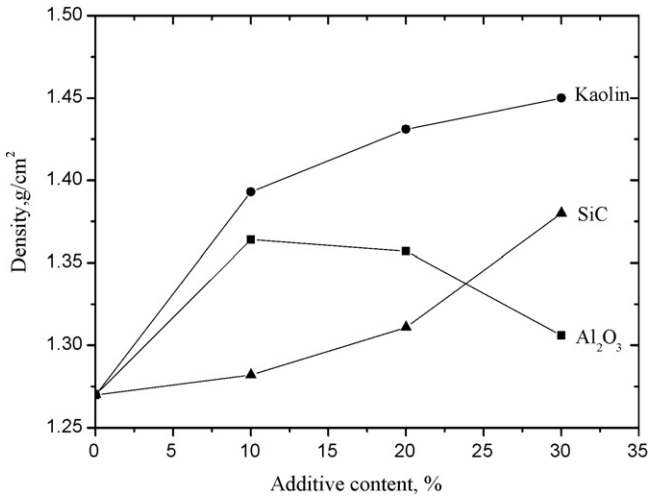

Fig. 9. Effect of the additives on densities of the TiB_2/Al_2O_3 composite.

The density of the TiB_2–Al_2O_3 composite is improved with adding 10 wt.% Al_2O_3 in green compact of the reaction powders. The addition of 10 wt.% Al_2O_3 reduces heat generation of the combustion reaction and the content of H_3BO_3 in the green compact, so less vapor is released at lower temperatures with reduced reaction rate. Furthermore, the cavities in the sintered body can be filled to some degree by the flow of Al_2O_3 at the adiabatic temperature above its liquidus. Further increase in Al_2O_3 addition reduces the density of the TiB_2–Al_2O_3 composite due to less amount of liquid Al_2O_3 present at their corresponding adiabatic temperature as indicated in Table 1.

By adding SiC, the density of the sintered ceramic composite is increased with raising SiC content, though the improvement is not prodigious compared with the kaolin addition. The reason is mainly from the occurrence of liquid aluminum oxide and the better wettability between SiC and Al_2O_3 particles.

Among the three additives, kaolin addition improves the density of the sintered TiB_2–Al_2O_3 composite most. The reason is that even with the addition of 30 wt.%, the dissolution product

Table 2
Theoretical densities of the Al_2O_3–$3TiB_2$ composite with different additives[a].

Additive	Density (g/cm^3)			
	Addition (wt.%)			
	0	10	20	30
Al_2O_3	4.151	4.137	4.123	4.106
Kaolin	4.151	3.996	3.840	3.686
SiC	4.151	4.057	3.963	3.871

[a] $\rho_{Al_2O_3} = 3.99\,g/cm^3$; $\rho_{TiB_2} = 4.52\,g/cm^3$; $\rho_{Kaolin} = 2.6\,g/cm^3$; $\rho_{SiC} = 3.2\,g/cm^3$.

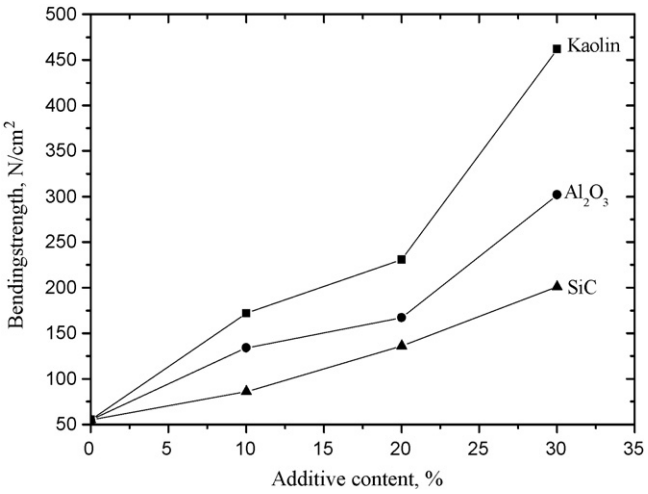

Fig. 10. Effect of additives on bending strength of the TiB_2/Al_2O_3 composite.

of kaolin, $3Al_2O_3{\cdot}2SiO_2$, is still in melt state with high fluidity because the adiabatic temperature is over 26.85 °C of its melting point. Therefore, the density of the TiB_2–Al_2O_3 composite is greatly increased by the flow and filling of the liquid $3Al_2O_3{\cdot}2SiO_2$ in cavities between the Al_2O_3 and TiB_2 particles although there is no presence of liquid Al_2O_3.

3.8. Bending strength of the TiB_2–Al_2O_3 composite

Without densification under pressure, the bending strength of the TiB_2–Al_2O_3 composite is only 55 N/cm^2. However, it is greatly improved by the addition of all the additives, as shown in Fig. 10. The SiC addition has the smallest contribution to bending strength of the composite due to its mere role as filler at the adiabatic temperature well below its melting point.

In the case of adding Al_2O_3, the bending strength of the composite is increased with more Al_2O_3 addition. The reason for the rise of bending strength of the TiB_2–Al_2O_3 composite with more Al_2O_3 addition is that the tendency to generate cracks in the sintered ceramics is reduced; although the densities of the sintered bodies are lower.[30]

The bending strength of the ceramic composite is increased dramatically with increasing kaolin content, and the addition of 30 wt.% kaolin produces the highest bending strength of 462 N/cm^2. This is more than seven times greater than the bending strength without any additive addition. The greatly enhanced bending strength of the composite comes from the relatively good fluidity and wettability of liquid kaolin with TiB_2 and Al_2O_3 at the combustion reaction temperatures.

4. Conclusions

Through studying the use of H_3BO_3 as a boron source, the effects of Al_2O_3, SiC and kaolin addition on the combustion synthesis of Al_2O_3–TiB_2 ceramics are drawn as follows.

Based on the first law of thermodynamics and from theoretical calculation, the adiabatic temperature of Al–TiO_2–H_3BO_3 system is 2314.85 °C. With the addition of Al_2O_3, kaolin and SiC, the adiabatic temperature of the reaction system is decreased with the increase in the additive addition.

With Al_2O_3 addition, the phases presented in the ceramic composite are TiB_2 and Al_2O_3, and the phases of SiC and $3Al_2O_3{\cdot}2SiO_2$ emerges when SiC and kaolin are added to the reaction system, respectively. Furthermore, all the additives have a refinement effect on the TiB_2 particulate.

Combustion wave velocity is rapidly decreased with increasing the additive additions. At given amounts of additives, the fastest combustion velocity happens in adding SiC, and the lowest one occurs in kaolin addition.

The density of the TiB_2–Al_2O_3 composite is improved with the addition of the additives. Furthermore, the highest density is obtained by adding 30 wt.% kaolin. With the Al_2O_3 and SiC additions, volumes of the sintered body are greater than those of the green compacts, while the addition of kaolin from 10 to 30 wt.% makes the volume changes from −4.6 to −1.2%.

The bending strength of the TiB_2–Al_2O_3 composite is only 55 N/cm^2 under combustion synthesis, and it is improved greatly by the addition of all the additives. A bending strength of 462 N/cm^2 is reached with the addition of 30 wt.% kaolin.

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