Metallothermic Combustion Reaction on Synthesis of Titanium Boride-Spinel Composites

Chun-Liang Yeh, Fu-You Zheng
Department of Aerospace and Systems Engineering, Feng Chia University
Taichung, Taiwan

1 Introduction

TiB₂ has been one of the most studied ultra-high temperature ceramics (UHTCs) due to its unique properties, including a high melting point (3225 °C), high hardness (33 MPa), high Young’s modulus (530 MPa), excellent wear and oxidation resistance, thermal shock resistance, chemical inertness, and good electric conductivity [1]. Combination of these properties makes TiB₂ an ideal candidate for use in ballistic armors, crucibles, metal evaporation boats, cutting tools, wear resistance parts, and cathodes for alumina smelting [1]. Many ceramic phases, such as Al₂O₃, SiC, B₄C, and MgAl₂O₄, have been considered as the reinforcement to improve fracture toughness, oxidation resistance, heat resistance, and mechanical strength of the TiB₂-based composites [1-3]. Magnesium aluminate spinel, MgAl₂O₄, as an additive has been rarely studied, possibly because the fabrication of MgAl₂O₄ via either the direct solid-state reaction of oxides or wet chemical methods requires multiple steps that are complicated and time-consuming [4,5]. However, MgAl₂O₄ is an attractive component due to its high melting point, chemical inertness, high hardness, corrosion resistance, high mechanical strength, and low cost [4].

Among various fabrication routes for preparing multiphasic ceramics, metallothermic reduction reactions (i.e., thermite reactions) combined with combustion synthesis have been recognized as a promising technique for in situ formation of MgAl₂O₄-containing composites. Combustion synthesis in the mode of self-propagating high-temperature synthesis (SHS), which is based on strongly exothermic reactions, has merits of low energy consumption, short reaction time, simple operation and equipment, high-purity products, and in situ formation of composite components [6]. Moreover, aluminothermic and magnesiothermic reduction reactions have Al₂O₃ and MgO as their respective by-products, both of which are precursors for the formation of MgAl₂O₄. Consequently, Omran et al. [7] applied the reduction-based SHS technique to produce MgAl₂O₄–W–W₂B composites through magnesiothermic reduction of WO₃ and B₂O₃ in the presence of Al₂O₃. Zaki et al. [8] synthesized MoSi₂– and Mo₃Si₃–MgAl₂O₄ composites by SHS with a reducing stage from raw materials consisting of MoO₃, SiO₂, and Al as aluminothermic reagents and MgO as a precursor.

This study represents the first attempt to prepare TiB₂–MgAl₂O₄ in situ composites from the SHS powder metallurgy simultaneously involving aluminothermic and magnesiothermic reduction of TiO₂ or B₂O₃. Only a small amount of Al₂O₃ or MgO was included in the reactive mixture to serve as the combustion moderator and part of the precursors for the formation of MgAl₂O₄. Four SHS reaction
systems formulated with different metallothermic reagents and combustion diluents were investigated. In this work, combustion exothermicity and combustion wave kinetics of the SHS process, as well as compositions and microstructures of the final products were explored.

2 Experimental Methods of Approach

The starting materials adopted by this study included TiO₂ (Acros Organics, 99.5%), B₂O₃ (Acros Organics, 99%), Al₂O₃ (Alfa Aesar, 99%), MgO (Acros Organics, 99.5%), Al (Showa Chemical Co., < 45 μm, 99.9%), Mg (Alfa Aesar, < 45 μm, 99.8%), and amorphous boron (Noah Technologies, < 1 μm, 93.5%). Four SHS reactions were formulated for the synthesis of 3TiB₂–MgAl₂O₄ composites. Two metallothermic reagents (i.e., thermites) were considered; one is composed of TiO₂, Al, and Mg, as shown in R(1) and R(2), and the other comprises B₂O₃, Al, and Mg, as in R(3) and R(4). Due to strong exothermicity of combustion, Al₂O₃ with an amount of 0.3 mol. was included in R(1) and R(3) as the combustion moderator (or combustion diluent) in order to attain stable propagation of the combustion wave. The pre-added Al₂O₃ also acted as part of the precursor for the synthesis of MgAl₂O₄. Likewise, an equal amount of MgO was adopted by R(2) and R(4) and MgO played the same role as Al₂O₃ in R(1) and R(3).

\[
\begin{align*}
\text{R(1)} & : (1.55\text{TiO}_2 + 1.4\text{Al} + 1.4\text{Mg}) + 0.3\text{Al}_2\text{O}_3 + 1.45\text{Ti} + 6\text{B} \rightarrow 3\text{TiB}_2 + \text{MgAl}_2\text{O}_4 \\
\text{R(2)} & : (1.85\text{TiO}_2 + 2\text{Al} + 0.7\text{Mg}) + 0.3\text{MgO} + 1.15\text{Ti} + 6\text{B} \rightarrow 3\text{TiB}_2 + \text{MgAl}_2\text{O}_4 \\
\text{R(3)} & : (1.033\text{B}_2\text{O}_3 + 1.4\text{Al} + 1.4\text{Mg}) + 0.3\text{Al}_2\text{O}_3 + 3\text{Ti} + 3.93\text{B} \rightarrow 3\text{TiB}_2 + \text{MgAl}_2\text{O}_4 \\
\text{R(4)} & : (1.233\text{B}_2\text{O}_3 + 2\text{Al} + 0.7\text{Mg}) + 0.3\text{MgO} + 3\text{Ti} + 3.53\text{B} \rightarrow 3\text{TiB}_2 + \text{MgAl}_2\text{O}_4
\end{align*}
\]

Combustion exothermicity of the above four reactions was evaluated by calculating their adiabatic combustion temperatures \(T_{ad}\) from the following energy balance equation [9] with thermochemical data taken from [10].

\[
\Delta H_r + \int_{298}^{T_{ad}} n_j c_p(P_j)dT + \sum_{298-T_{ad}} n_j L(P_j) = 0
\]

where \(\Delta H_r\) is the reaction enthalpy at 298 K, \(n_j\) is the stoichiometric coefficient, \(c_p\) and \(L\) are the heat capacity and latent heat, and \(P_j\) refers to the product component.

The SHS experiments were conducted in a windowed combustion chamber under argon of 0.25 MPa. Reactant powders were well mixed in a ball mill and uniaxially compressed into cylindrical test specimens with a diameter of 7 mm, a height of 12 mm, and a relative density of 55%. The ignition of sample compacts was achieved by an electrically heated tungsten coil. The combustion wave propagation velocity \(V_f\) was determined by the time derivative of the flame-front trajectory constructed from the recorded series of combustion images. The combustion temperature was measured by the R-type (Pt/Pt-13%Rh) bare-wire thermocouple with a bead size of 125 μm. Phase compositions of the products were identified by an X-ray diffractometer (XRD, Bruker D2 Phaser). Microstructures and constituent elements of the products were examined by the scanning electron microscopy (SEM, Hitachi, S3000H) and energy dispersive spectroscopy (EDS). Details of the experimental methods were reported elsewhere [11].

3 Results and Discussion

Figure 1 presents the calculated \(\Delta H_r\) and \(T_{ad}\) of reactions R(1)-R(4) and shows that R(4) has the highest values while R(1) has the lowest ones. Both \(\Delta H_r\) and \(T_{ad}\) increases from R(1) to R(4). Specifically, the values of \(T_{ad}\) are 2530 K, 2595 K, 2783 K, 2897 K for R(1), R(2), R(3), and R(4), respectively. A
comparison between R(1) and R(2) revealed that the combustion moderator Al₂O₃ appeared to impose a stronger dilution effect on combustion than MgO, which led to a lower $T_{ad}$ for R(1) than R(2). Similar results were observed in R(3) and R(4). These findings could also be explained by the fact that metallothermic reduction of TiO₂ or B₂O₃ by Al is more exothermic than that by Mg [10].

On the other hand, because the B₂O₃-based thermite is more energetic than the one using TiO₂ [10], R(3) has a higher $T_{ad}$ than R(1). Similarly, R(4) has a higher $T_{ad}$ than R(2). According to the calculated $T_{ad}$, it is realized that the thermite oxidants (i.e., B₂O₃ versus TiO₂) have a more pronounced influence on combustion exothermicity than the diluent oxides (i.e., Al₂O₃ versus MgO).

Figure 1: Enthalpies of reaction ($\Delta H_r$) and adiabatic combustion temperatures ($T_{ad}$) of SHS reactions.

Two series of the SHS processes recorded from reactions R(1) and R(3) are illustrated in Figure 2(a) and (b), respectively. It is apparent that upon ignition, the reaction was initiated and characterized by a self-sustaining combustion wave. More intense combustion accompanied with a faster combustion wave was observed in Figure 2(b), when compared with that in Figure 2(a). Combustion luminosity and flame spreading speed reflected the degree of reaction exothermicity. As mentioned above, B₂O₃/Al/Mg-based R(3) is more energetic than TiO₂/Al/Mg-based R(1). Similar combustion behavior was also noticed in R(2) and R(4).

Figure 2: Time sequences of recorded SHS images illustrating self-sustaining combustion wave of (a) R(1) and (b) R(3).

Figure 3 depicts typical combustion temperature profiles measured from four different reactions. All profiles exhibit a steep thermal gradient followed by a rapid descent, which is inherent in the SHS reaction that features a rapid combustion wave and a thin reaction zone. The peak value is considered as the combustion front temperature ($T_c$). When compared with pinnacles in the contours of R(1) and R(2), sharper peaks were detected in the profiles of R(3) and R(4) This implied a faster combustion wave in R(3) and R(4). As shown in Figure 3, the values of $T_c$ from R(1) to R(4) in ascending order are 1348 °C, 1445 °C, 1660 °C, and 1736 °C. It should be noted that the measured combustion front temperatures are in agreement with the calculated reaction exothermicity.

Figure 4 plots the measured combustion wave propagation velocities ($V_f$) and temperatures ($T_c$) of four reactions. The rising trend of $V_f$ from R(1) to R(4) is consistent with that of $T_c$. This can be explained...
by the fact that combustion wave propagation is essentially governed by layer-by-layer heat transfer from the thin combustion zone to unreacted region, and therefore, is subject to the reaction front temperature. As presented in Figure 4, the average combustion velocities are 3.9, 4.7, 5.1, and 5.7 mm/s for R(1), R(2), R(3), and R(4), respectively. It is worth noting that the measured combustion temperature not only justified the reaction exothermic analysis, but also confirmed the temperature dependence of combustion wave velocity.

The XRD spectra of the final products synthesized from R(1) and R(2) are shown in Figure 5(a) and (b), respectively. Both indicated the formation of TiB₂ and MgAl₂O₄ along with two minor phases, magnesium titanate (MgTiO₃) and MgO. It is believed that MgAl₂O₄ was synthesized through a combination reaction between Al₂O₃ and MgO. R(1) and R(2) were formulated with the same thermite reagents of TiO₂, Al, and Mg, but diluted by different metal oxides. That is, Al₂O₃ was partly pre-added and partly thermite-produced, while MgO was all generated from the reduction of TiO₂ by Mg in R(1). In contrast, the required Al₂O₃ in R(2) was entirely produced from the reduction of TiO₂ by Al, but MgO was supplied in part from prior addition and in part from the reduction of TiO₂ by Mg. For both R(1) and R(2), TiB₂ was synthesized from the reaction of elemental boron with reduced and metallic Ti. Traces of MgO suggested an incomplete reaction due probably to the relatively low reaction temperatures of R(1) and R(2). The presence of MgTiO₃ in the final products of R(1) and R(2) could be attributed to the reaction of MgO with the thermite oxidant TiO₂.

Figure 6(a) and (b) exhibits the XRD patterns of the synthesized composites from R(3) and R(4), respectively. In addition to TiB₂ and MgAl₂O₄, a small amount of MgTiO₃ was identified. The formation of MgAl₂O₄ from a combination reaction between Al₂O₃ and MgO was proved. Both Al₂O₃ and MgO can be totally or partially produced from the reduction of B₂O₃ by Al and Mg. For R(3) and R(4) containing B₂O₃/Al/Mg-based thermite, TiB₂ was produced from the reaction of metallic Ti with reduced and elemental boron. Moreover, the formation of MgTiO₃ in R(3) and R(4) might involve some interaction of Ti with B₂O₃ to form TiO₂ which further reacted with MgO. Unlike that in R(1) and R(2), MgO was no longer detected in the final products of R(3) and R(4).

The microstructure of fracture surface of the synthesized product of R(1) shows several large and solidified MgAl₂O₄ aggregates of 5–15 μm surrounded by fine-grain TiB₂ crystals with a particle size of about 1–2 μm. For the final product of B₂O₃/Al/Mg-based R(4), the microstructure and atomic ratios of constituent elements are presented in Figure 7. As can be seen, MgAl₂O₄ was formed as large densified aggregates of around 20 μm and TiB₂ crystals were in a short-rod form with a length of 2–4 μm or in a shape of fine grains of 1–2 μm. Based on the EDS analysis, the atomic ratio of the selected
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area in an aggregate is Mg:Al:O = 15.1:30.6:54.3 that is reasonably close to MgAl₂O₄. Short-rod crystals have a composition of Ti:B = 34.3:65.7, which certainly is TiB₂.

Figure 5: XRD patterns of final products of (a) R(1) and (b) R(2).

Figure 6: XRD patterns of final products of (a) R(3) and (b) R(4).

Figure 7: SEM micrograph and EDS spectra of TiB₂/MgAl₂O₄ composite synthesized from R(4).

4 Conclusion

In situ formation of 3TiB₂–MgAl₂O₄ composites was conducted by combustion synthesis combined with metallothermic reduction reactions involving Al and Mg as dual reductants. Thermit reagents with different oxidants were considered; one utilized TiO₂ and the other B₂O₃. The reactant mixtures also contained elemental Ti and boron. The overall synthesis reaction was exothermic enough to proceed in the SHS mode. The analysis of combustion exothermicity indicated that the SHS reaction containing B₂O₃/Al/Mg-based thermites was more energetic than that adopting TiO₂ as the oxidant. Prior addition of Al₂O₃ had a stronger dilution effect on combustion than that of MgO. Depending on
different thermites and diluents, the measured combustion front temperatures ranged from 1320 to 1720 °C, and combustion wave velocity from 3.9 to 5.7 mm/s. The temperature dependence of combustion wave velocity was justified. The XRD analysis confirmed in situ formation of TiB$_2$ and MgAl$_2$O$_4$. A small amount of MgTiO$_3$ was found as the impurity. It is believed that MgAl$_2$O$_4$ was synthesized through a combination reaction between Al$_2$O$_3$ and MgO, both of which can be totally or partially produced from the metallothermic reduction of B$_2$O$_3$ or TiO$_2$. The microstructure of the synthesized composite exhibited that MgAl$_2$O$_4$ was surrounded by closely-packed TiB$_2$ grains. MgAl$_2$O$_4$ was formed as densified aggregates with a size of 5-20 µm. TiB$_2$ crystals were produced in a shape of short rods of 2–4 µm and fine grains of 1–2 µm. An energy-saving and efficient fabrication route for the formation MgAl$_2$O$_4$-containing composites was demonstrated by this study.

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References


