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# In Situ Formation of TiB<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-Reinforced Fe<sub>3</sub>Al by Combustion Synthesis with Thermite Reduction

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**Abstract:** Fabrication of Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composites with a broad range of phase compositions was studied by combustion synthesis involving aluminothermic reduction of oxide precursors. Two reaction systems composed of elemental Fe, amorphous boron, and a thermite mixture of Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/Al were conducted in the mode of self-propagating high-temperature synthesis (SHS). One was to produce the composites of 1.25Fe<sub>3</sub>Al + *x*TiB<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> with *x* = 0.3–1.0. The other was to fabricate the products of *y*Fe<sub>3</sub>Al + 0.6TiB<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> with *y* = 1.0–1.6. Reduction of Fe<sub>2</sub>O<sub>3</sub> by Al acted as an initiation step to activate the SHS process. Complete phase conversion from the reactants to Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composites was achieved. The variation of combustion front velocity with sample stoichiometry was consistent with that of the reaction exothermicity. Based on combustion wave kinetics, the activation energy of  $E_a = 86.8 \text{ kJ/mol}$  was determined for formation of the Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composite through the thermite-based SHS reaction. In addition, with an increase in TiB<sub>2</sub>, the fracture toughness of the 1.25Fe<sub>3</sub>Al + *x*TiB<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> composite was found to increase from 5.32 to 7.92 MPa·m<sup>1/2</sup>.

**Keywords:** self-propagating high-temperature synthesis (SHS); iron aluminides; Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composites; aluminothermic reduction; activation energy

## 1. Introduction

The iron aluminides Fe<sub>3</sub>Al and FeAl have been of significant importance for high-temperature structural and coating applications due to their low cost, low density, relatively high melting point, high electrical resistivity, and good oxidation, corrosion, and sulfidation resistance. However, they exhibit low ductility and brittle fracture at ambient temperatures [1–3]. Efforts to strengthen iron aluminides showed that the room-temperature strength and wear resistance of Fe<sub>3</sub>Al were greatly improved by incorporating hard carbide or boride particles (such as TiC, WC, TiB<sub>2</sub>, and ZrB<sub>2</sub>) [4–7]. Also, oxide ceramics are effective in reinforcing iron aluminides. The addition of Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> particles can enhance the high-temperature strength of Fe<sub>3</sub>Al without compromising its oxidation resistance [8–11].

A variety of processing techniques have been employed to fabricate iron aluminide–ceramic composites, including liquid-phase sintering [4], hot pressing [8,9], mechanochemical synthesis [10], solid-state displacement reactions [11], and combustion synthesis in the modes of self-propagating high-temperature synthesis (SHS) [12] and thermal explosion [13]. Among them, the SHS method takes advantage of highly exothermic reactions, and hence has the merits of a low energy requirement, a short reaction time, inexpensive equipment, simplicity of operation, and a structural and functional diversity of final products [14–16]. When combined with a thermite reaction using Al as the reducing agent, combustion synthesis represents an in situ fabrication route to prepare Al<sub>2</sub>O<sub>3</sub>-reinforced intermetallics

and ceramics [12,13,17,18]. Moreover, aluminothermic reduction of metal oxides is thermally beneficial for the SHS process.

Preparation of transition-metal aluminides of the Ni–Al and Ti–Al systems has been studied by the classical SHS method using elemental powder compacts of their corresponding stoichoimetries [19–21]. However, direct combustion between Fe and Al powders in a compressed form to produce Fe<sub>3</sub>Al and FeAl is not feasible because of their low formation enthalpies or high activation energy barrier. As a result, few related studies on combustion synthesis of iron aluminides are available. According to Sharifitabar et al. [12], TiC/Al<sub>2</sub>O<sub>3</sub>-added Fe<sub>3</sub>Al was produced by combustion synthesis in the SHS mode from a  $3TiO_2 + 4Al + 3C$  exothermic mixture with an addition of Fe. Liu et al. [13] obtained FeAl/Al<sub>2</sub>O<sub>3</sub> composites from a reactant mixture made up of Fe, Al, and Fe<sub>2</sub>O<sub>3</sub> by thermal explosion of combustion synthesis. The ignition temperatures were between 639 and 648 °C and the products were highly porous [13].

This study aims to investigate in situ formation of  $TiB_2/Al_2O_3$ -reinforced Fe<sub>3</sub>Al composites by the SHS method involving aluminothermic reduction of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. In addition to the thermite reagents, the starting materials included elemental iron and amorphous boron powders. Effects of TiB<sub>2</sub> and Fe<sub>3</sub>Al contents on combustion characteristics were studied. The activation energy of the Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-Al-Fe–B combustion system was deduced from the measured combustion wave velocity and temperature. Moreover, the strengthening effect of TiB<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> on Fe<sub>3</sub>Al was examined.

#### 2. Materials and Methods

The starting materials of this study included Fe<sub>2</sub>O<sub>3</sub> (Alfa Aesar Co., <45  $\mu$ m, 99.5%, Ward Hill, MA, USA), TiO<sub>2</sub> (Alfa Aesar Co., 1–2  $\mu$ m, 99.5%), Al (Showa Chemical Co., <45  $\mu$ m, 99.9%, Tokyo, Japan), Fe (Alfa Aesar Co., <45  $\mu$ m, 99.5%), and amorphous boron (Noah Technologies Corp., <1  $\mu$ m, 92%, San Antonio, TX, USA). Two combustion systems adopting TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Al as the thermite reagents were prepared. Reaction (1) has a variable molar ratio of TiO<sub>2</sub> to Fe<sub>2</sub>O<sub>3</sub> and is to produce Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composites with different contents of TiB<sub>2</sub>. On the other hand, the molar proportion between the two oxide precursors is fixed and equal to unity in Reaction (2) and the resulting composites contain different amounts of Fe<sub>3</sub>Al.

$$x \operatorname{TiO}_2 + \left(1 - \frac{2x}{3}\right) \operatorname{Fe}_2 \operatorname{O}_3 + \frac{13}{4} \operatorname{Al} + \left(\frac{7}{4} + \frac{4x}{3}\right) \operatorname{Fe} + 2x \operatorname{B} \to 1.25 \operatorname{Fe}_3 \operatorname{Al} + x \operatorname{TiB}_2 + \operatorname{Al}_2 \operatorname{O}_3$$
 (1)

$$\frac{3}{5}\text{TiO}_2 + \frac{3}{5}\text{Fe}_2\text{O}_3 + (y+2)\text{Al} + \left(3y - \frac{6}{5}\right)\text{Fe} + \frac{6}{5}\text{B} \to y\text{Fe}_3\text{Al} + 0.6\text{TiB}_2 + \text{Al}_2\text{O}_3 \tag{2}$$

where the stoichiometric coefficients, *x* and *y*, signify the molar contents of TiB<sub>2</sub> and Fe<sub>3</sub>Al formed in Fe<sub>3</sub>Al/TiB<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> composites based upon Reactions (1) and (2), respectively. Reactant mixtures were formulated with  $0.3 \le x \le 1.0$  in Reaction (1) and  $1.0 \le y \le 1.6$  in Reaction (2) to attain stable and self-sustaining combustion.

The reactant powders were well-mixed and compressed into cylindrical samples that were 7 mm in diameter, 12 mm in length, and had a relative density of 60%. The SHS reaction was conducted in a windowed stainless-steel chamber under high purity argon (99.99%) of 0.15 MPa. The combustion wave velocity ( $V_f$ ) was deduced from the time sequence of recorded images. The combustion temperature ( $T_c$ ) was measured by a fine-wire (125 µm) Pt/Pt-13%Rh thermocouple attached on the sample surface. Phase constituents of the final product were identified by carrying out phase analyses based on the measured powder X-ray diffraction patterns (Bruker D2) using CuK<sub> $\alpha$ </sub> radiation with  $\lambda$  = 1.5406 Å. The measured XRD patterns were corrected against an external silicon standard. FullProf software (FullProf, Saclay, France) was used for the processing of the data and analyses of the X-ray diffraction patterns. The FullProf program has been mainly developed for the Rietveld analysis of neutron (constant wavelength, time of flight, and nuclear and magnetic scattering) or X-ray powder diffraction data collected at a constant or variable step in scattering angle 20 [22,23]. The program can be used as

a profile matching (or pattern decomposition using the Le Bail method) tool without knowledge of the structure. Single crystal refinement can also be performed alone or in combination with powder data [23]. The microstructure of the synthesized product was examined under a scanning electron microscope (SEM) (Hitachi, S3000H, Tokyo, Japan) and elemental analysis was performed by energy dispersive spectroscopy (EDS) (Hitachi, S3000H, Tokyo, Japan). The fracture toughness ( $K_{IC}$ ) of the SHS-derived composite was determined by the indentation method [24]. Details of the experimental methods were previously reported [25].

#### 3. Results and Discussion

#### 3.1. Self-Propagating Combustion Characteristics and Kinetics

Figure 1 presents a typical combustion sequence recorded from the sample of Reaction (1) with x = 0.5. It is evident that upon ignition a distinct combustion wave forms and propagates over the starting reactant compact in a self-sustaining manner. Namely, the synthesis reaction proceeds in a form of combustion wave and yields the final product progressively without requiring additional heat. It took about t = 1.8 s for the combustion wave to arrive at the bottom of the sample. With an optically superimposed scale on the left-hand side of each image, the flame-front propagation velocity was determined.



**Figure 1.** A time sequence of self-propagating combustion images recorded from a powder compact of Reaction (1) with x = 0.5.

It is useful to note that the thermite reaction of Fe<sub>2</sub>O<sub>3</sub> + 2Al ( $\Delta H = -852.3$  kJ and  $T_{ad} = 3622$  K) is much more exothermic than that of 1.5TiO<sub>2</sub> + 2Al ( $\Delta H = -258.7$  kJ and  $T_{ad} = 1799$  K) [26,27]. Therefore, the reaction exothermicity of overall aluminothermic reduction decreases with the increase of x in Reaction (1). It was found in this study that due most likely to insufficient reaction exothermicity, combustion ceased to proceed in Reaction (1) with x > 1.0. On the contrary, violent combustion accompanying massive melting of the sample occurred in Reaction (1) with x < 0.3, which made both experimental measurement and product recovery difficult.

In Reaction (2), the increase of Fe and Al (i.e., the coefficient *y*) for the production of more Fe<sub>3</sub>Al imposes a dilution effect on combustion, because the formation enthalpy of Fe<sub>3</sub>Al ( $\Delta H_f = -67 \text{ kJ/mol}$ ) is much lower than those of TiB<sub>2</sub> ( $\Delta H_f = -315.9 \text{ kJ/mol}$ ) and Al<sub>2</sub>O<sub>3</sub> ( $\Delta H_f = -1675.7 \text{ kJ/mol}$ ) [1,27]. The combustibility limit of Reaction (2) was found at *y* = 1.6, beyond which no combustion can be triggered.

For both combustion systems, formation of the  $Fe_3Al-TiB_2-Al_2O_3$  composite proceeds in three consecutive stages [26]. Reduction of  $Fe_2O_3$  by Al to produce Fe and  $Al_2O_3$  is believed to be the initiation step, which is followed by aluminothermic reduction of  $TiO_2$ . Then, the interactions of Fe with Al and Ti with B respectively yield  $Fe_3Al$  and  $TiB_2$ .

Variations of the flame-front velocity of Reactions (1) and (2) are shown in Figure 2 with respect to their corresponding stoichiometric coefficients x and y. As revealed in Figure 2, the combustion front velocity of Reaction (1) first increases with x, approaches to a maximum of about 5.88 mm/s at x = 0.6, and then decreases with a further increase in x. This is because the influence of the

sample stoichiometry of Reaction (1) on combustion velocity is attributed to two competing factors. With the increase of *x*, the amount of TiO<sub>2</sub> increases but that of Fe<sub>2</sub>O<sub>3</sub> deceases in the starting mixture, thus resulting in a decline in reaction exothermicity of the overall aluminothermic reduction. On the other hand, the content of TiB<sub>2</sub> formed in the product increases as the coefficient *x* rises and TiB<sub>2</sub> is a highly exothermic phase with  $\Delta H_f = -315.9 \text{ kJ/mol}$  [27]. The observation in Figure 2 for Reaction (1) implies that the latter concern governs when the sample stoichiometry varies from *x* = 0.3 to 0.6, beyond which the former factor becomes dominant. As a result, the flame-front velocity dropped to around 1.02 mm/s at *x* = 1.0.



**Figure 2.** Effects of stoichiometric coefficients (*x* and *y*) on flame-front velocities of Reactions (1) and (2) for combustion synthesis of  $Fe_3Al-TiB_2-Al_2O_3$  composites.

Figure 2 also points out that the combustion wave speed of Reaction (2) decreases with increasing y value. The increase of y in Reaction (2) is to enlarge the content of Fe<sub>3</sub>Al formed from metallic Fe and Al without varying the composition of thermite reagents and the amount of TiB<sub>2</sub>. As mentioned above, the formation enthalpy of Fe<sub>3</sub>Al is relatively low in comparison to that of TiB<sub>2</sub> and the heat released from the reduction of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> by Al. Therefore, the increase of y from 1.0 to 1.6 reduced the overall combustion exothermicity of Reaction (2) and led to deceleration of the combustion wave from 6.23 to 1.69 mm/s.

Typical combustion temperature profiles recorded from the powder compacts of Reactions (1) and (2) with different stoichiometries are depicted in Figure 3. The abrupt rise in temperature signifies a rapid arrival of the combustion wave and the peak value corresponds to the combustion front temperature. After the passage of the combustion wave, an appreciable temperature drop is a consequence of heat loss to the surroundings. Profiles #1, #2, and #3 in Figure 3 are associated with Reaction (1) with x = 0.3, 0.6, and 0.8 and their peak temperatures are 1157, 1514, and 1277 °C, respectively. This suggests that the variation of combustion front temperature of Reaction (1) with TiB<sub>2</sub> content is in a manner consistent with that of flame-front velocity. For Reaction (1), the highest combustion front temperature of 1514 °C was detected from the sample of x = 0.6.



**Figure 3.** Variations of combustion temperature with TiB<sub>2</sub> and Fe<sub>3</sub>Al contents of Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composites synthesized by self-propagating high-temperature synthesis (SHS) involving reduction reactions.

Profiles #4 and #5 were measured from Reaction (2) with y = 1.4 and 1.6, respectively. It is evident that the increase of Fe<sub>3</sub>Al lowers the reaction temperature, which is in agreement with its effect on combustion wave velocity. For Reaction (2), the lowest combustion front temperature was around 1061 °C as the sample produced the maximum amount of Fe<sub>3</sub>Al (i.e., y = 1.6). The highest temperature, reaching up to 1524 °C, was observed in the sample of y = 1.0.

The apparent activation energy ( $E_a$ ) of the solid-state combustion reaction can be deduced by realizing the dependence of flame-front velocity on combustion temperature [28]. Figure 4 depicts a plot correlating  $\ln(V_f/T_c)^2$  with  $1/T_c$  from both Reactions (1) and (2). According to the slope of a best-fitted straight line for the data,  $E_a = 86.8$  kJ/mol was determined for in situ formation of Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composites from the Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/Al/Fe/B combustion reaction. It is useful to note that the activation energy obtained in the present study is close to that of the Fe<sub>2</sub>O<sub>3</sub>–Al reaction ( $E_a = 83.1$  kJ/mol) [29]. This implies that aluminothermic reduction of Fe<sub>2</sub>O<sub>3</sub> plays an important role in leading and facilitating the reaction sequences of the Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/Al/Fe/B combustion system.



**Figure 4.** Correlation of combustion front velocity ( $V_f$ ) with temperature ( $T_c$ ) for determination of the activation energy ( $E_a$ ) of Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/Al/Fe/B combustion to produce Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composites.

#### 3.2. Phase Constituents and Properties of Synthesized Composites

Figure 5a,b displays the XRD patterns of the final products fabricated from Reaction (1) with x = 0.5 and 0.8, respectively. The as-synthesized products composed of Fe<sub>3</sub>Al, TiB<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> were identified [30]. Figure 5 reveals that with the increase of x the relative intensity of signature peaks of TiB<sub>2</sub> becomes stronger, which is indicative of an increase in TiB<sub>2</sub> formed in the composite.



**Figure 5.** XRD patterns of SHS-derived products from Reaction (1) with (a) x = 0.5 and (b) x = 0.8.

The phase composition of SHS-derived products from Reaction (2) is presented in Figure 6a,b for y = 1.0 and 1.5, respectively. Complete conversion from the reactants to products of Fe<sub>3</sub>Al, TiB<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> was achieved. The characteristic peaks of Fe<sub>3</sub>Al in Figure 6b exhibit much higher intensity than those in Figure 6a. This confirms that more Fe<sub>3</sub>Al was produced from the SHS process as Reaction (2) contains additional metallic Fe and Al. In summary, the composition range of the TiB<sub>2</sub> / Al<sub>2</sub>O<sub>3</sub>-added Fe<sub>3</sub>Al composites produced in this study can be described by yFe<sub>3</sub>Al + xTiB<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> with x = 0.3–1.0 and y = 1.0–1.6.



**Figure 6.** XRD patterns of SHS-derived products from Reaction (2) with (a) y = 1.0 and (b) y = 1.5.

The relative fraction of constituents was analyzed by the Rietveld refinement for two selected SHS-derived products. The measured lattice parameters (**a** and **c**) of Fe<sub>3</sub>Al, TiB<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> are reported in Table 1. For the composite of  $1.25Fe_3Al + 0.8TiB_2 + Al_2O_3$  synthesized from Reaction (1), the Rietveld method indicates that the weight percentages are 61.88 wt % of Fe<sub>3</sub>Al, 3.72 wt % of TiB<sub>2</sub>, and 24.40 wt % of Al<sub>2</sub>O<sub>3</sub>. The relative fractions of Fe<sub>3</sub>Al (65.98 wt %), TiB<sub>2</sub> (9.56 wt %), and Al<sub>2</sub>O<sub>3</sub> (24.46 wt %) are determined for the composite of  $1.5Fe_3Al + 0.6TiB_2 + Al_2O_3$  obtained from Reaction (2). It is useful to note that the results of the Rietveld method for the phase composition are in good agreement with those of Reactions (1) and (2).

Composites	Components	a (Å)	c (Å)
Reaction (1) with $x = 0.8$	Fe <sub>3</sub> Al TiB <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>	5.774 3.027 4.764	3.230 13.002
Reaction (2) with $y = 1.5$	Fe <sub>3</sub> Al TiB <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>	5.786 3.024 4.768	- 3.226 13.005

**Table 1.** Lattice parameters (a and c) for the components in two selected composites.

The typical microstructure of a fracture surface of the SHS-produced Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composite is displayed in Figure 7, which presents the product of Reaction (2) with y = 1.6. The microstructure exhibits the agglomeration of micro-sized grains. The agglomerates have a dense and contiguous morphology. For those gray agglomerates shown in Figure 7, the EDS analysis indicates their atomic ratio to be Fe:Al = 75.43:24.57, which matches well with that of Fe<sub>3</sub>Al. It is believed that most of the TiB<sub>2</sub> grains are embedded in the agglomerates. The other distinct morphology is characterized by bright alumina grains, whose atomic proportion determined by the EDS spectrum is Al:O = 37.34:62.66.



**Figure 7.** SEM micrograph and EDS spectra of the  $Fe_3Al-TiB_2-Al_2O_3$  composite synthesized from Reaction (2) with *y* = 1.6.

The hardness of the TiB<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-added Fe<sub>3</sub>Al composites synthesized from Reaction (1) is in the range from 11.2 to 19.6 GPa, which increases with increasing TiB<sub>2</sub> content from x = 0.3 to 1.0. Figure 8 shows that as the content of TiB<sub>2</sub> increases, the fracture toughness of the TiB<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-reinforced Fe<sub>3</sub>Al

composite increases from 5.32 to 7.92 MPa $\cdot$ m<sup>1/2</sup>. This proves the strengthening effect of the ceramic phases on Fe<sub>3</sub>Al.



**Figure 8.** Effect of TiB<sub>2</sub> content on the fracture toughness of 1.25Fe<sub>3</sub>Al + xTiB<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> composites synthesized by SHS of Reaction (1).

#### 4. Conclusions

The SHS process involving aluminothermic reduction of oxide precursors was conducted to prepare Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composites with a broad range of phase compositions. The starting materials included elemental Fe, amorphous boron, and thermite reagents made up of Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and Al. Aluminothermic reduction of Fe<sub>2</sub>O<sub>3</sub> played an important role in thermally and chemically activating the synthesis reaction in a self-sustaining combustion mode. Experimental results showed that for the production of a higher content of TiB<sub>2</sub> in the composites of 1.25Fe<sub>3</sub>Al + *x*TiB<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> with *x* = 0.3–1.0, there existed a maximum combustion wave velocity of 5.88 mm/s and a highest reaction front temperature of 1514 °C at *x* = 0.6. This was caused by the fact that the reaction exothermicity of the thermite mixture decreased but the formation enthalpy of TiB<sub>2</sub> increased. On the other hand, for the increase of Fe<sub>3</sub>Al in the product of *y*Fe<sub>3</sub>Al + 0.6TiB<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> with *y* = 1.0–1.6, the additional Fe and Al reduced the overall reaction exothermicity and decelerated the combustion wave. Based upon the dependence of flame-front velocity on combustion temperature, the activation energy (*E<sub>a</sub>*) of 86.8 kJ/mol was determined for the Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/Al/Fe/B combustion system to produce Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composites.

The XRD analysis of the as-synthesized products indicated that complete conversion from the reactants to Fe<sub>3</sub>Al–TiB<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composites was achieved. Two SHS systems capable of varying the molar contents of TiB<sub>2</sub> and Fe<sub>3</sub>Al in an effective manner were confirmed. Moreover, it was found that the increase of TiB<sub>2</sub> from x = 0.3 to 1.0 in the 1.25Fe<sub>3</sub>Al + xTiB<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> composites contributed to an increase in fracture toughness from 5.32 to 7.92 MPa·m<sup>1/2</sup>.

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