

Article Synthesis of FeSi-Al₂O₃ Composites by Autowave Combustion with Metallothermic Reduction

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Abstract: Fabrication of FeSi-Al₂O₃ composites with a molar ratio of FeSi/Al₂O₃ ranging from 1.2 to 4.5 was conducted by the self-propagating high-temperature synthesis (SHS) method. The synthesis reaction involved metallothermic reduction of Fe₂O₃ and SiO₂ by Al and the chemical interaction of Fe and Si. Two combustion systems were examined: one contained thermite reagents of $0.6Fe_2O_3 + 0.6SiO_2 + 2Al$, and the other had $Fe_2O_3 + 2Al$ to mix with different amounts of Fe and Si powders. A thermodynamic analysis indicated that metallothermic reduction of oxide precursors was sufficiently exothermic to sustain the combustion reaction in a self-propagating mode. The SHS reaction carrying out co-reduction of Fe₂O₃ and SiO₂ was less exothermic, and was applied to synthesize products with FeSi/Al₂O₃ = 1.2–2.5, while the reaction reducing only Fe₂O₃ was more energetic and was adopted for the composites with FeSi/Al₂O₃ = 2.5–4.5. Moreover, the former had a larger activation energy, i.e., $E_a = 215.3 \text{ kJ/mol}$, than the latter, i.e., $E_a = 180.4 \text{ kJ/mol}$. For both reaction systems, the combustion wave velocity and temperature decreased with increasing FeSi content. Formation of FeSi-Al₂O₃ in situ composites with different amounts of FeSi was achieved. Additionally, a trivial amount of aluminum silicate was detected in the products of high FeSi contents due to dissolution of Si into Al₂O₃ during the SHS process.

Keywords: FeSi-Al₂O₃ composite; Self-propagating High-temperature Synthesis (SHS); aluminothermic reduction; activation energy

1. Introduction

Transition metal silicides have been the focus of many investigations due to their attractive high-temperature properties and a wide range of potential applications. Within the Fe-Si system, iron silicide compounds include Fe₃Si, Fe₂Si, Fe₅Si₃, FeSi, β -FeSi₂, and α -FeSi₂ [1]. According to the phase diagram, Fe₃Si, FeSi, and β -FeSi₂ are stable at room temperature, while Fe₂Si, Fe₅Si₃, and α -FeSi₂ are metastable. Depending on their crystal structures, these iron silicides exhibit magnetic, semiconducting, insulating, and metallic behavior [2–4]. For example, Fe₃Si has a relatively high value of saturation magnetization and is a promising candidate as a ferromagnetic electrode [2]. FeSi has a high melting point, i.e., 1410 °C, good high-temperature structural stability, and excellent resistance to chemical corrosion, especially in harsh industrial environments [5]. Also, FeSi is a transitionmetal Kondo insulator and acts as the host structure for the ferromagnetic semiconducting β -FeSi₂ at low temperatures and tetragonal metallic α -FeSi₂ at high temperatures. β -FeSi₂ is a potential optoelectronic and thermoelectric material, owing to its direct band gap of 0.87 eV, with a wide range of absorption spectrum and relatively large Seebeck coefficient [7–9].

Among various methods for fabricating transition metal silicides, combustion synthesis in the mode of self-propagating high-temperature synthesis (SHS) has the advantages of energy efficiency, short processing time, low cost, and high purity of the product [10–12]. The SHS scheme has been extensively applied to synthesize many silicide compounds of the Ti-Si, Nb-Si, Zr-Si, Ta-Si, and Mo-Si systems from elemental powder compacts of



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). their corresponding stoichoimetries [13–17]. However, weak combustion exothermicity restrains the preparation of iron silicides from the direct SHS reaction between Fe and Si powders. Despite the fact that the reactions are exothermic, Fe + Si \rightarrow FeSi has an enthalpy of formation of $\Delta H_{\rm f} = -79.4 \text{ kJ/mol}$ and an adiabatic temperature of $T_{ad} = 1650 \text{ K}$ and Fe + 2Si \rightarrow FeSi₂ has $\Delta H_{\rm f}$ = -81.2 kJ/mol and T_{ad} = 1310 K [18]. It has been empirically concluded that the autowave synthesis reaction will not be achievable unless the adiabatic combustion temperature is higher than 1800 K [19]. As a consequence, several activation approaches have been employed. By using high-energy ball milling to mechanically activate the self-sustaining combustion of Fe + 2Si powder mixtures, Gras et al. [20,21] obtained FeSi as the main product for the operation conditions of short duration milling (1–4 h) and moderate shock power (2.2 W), while β -FeSi₂ was formed in the postcombustion zone for those of long duration milling (6 h) or high shock power (4.8 W). The role of 20 wt% KNO₃ as an additive to chemically activate the reactivity of Fe + 2Si mixtures was examined [22]. It was found that decomposition of KNO₃ generated enough thermal energy to assist the combustion reaction in a stable and self-sustaining mode, and that the resulting product consisted of FeSi and α -FeS₁₂ [22]. Moreover, the FeSi-Al₂O₃ composite was synthesized by the mechanical alloying of SiO_2 , Al, and Fe powders, and complete reduction of SiO_2 by Al was reached after 45 h of milling [23].

As the first attempt, this study aims to fabricate FeSi-Al₂O₃ composites by the SHS process involving metallothermic reduction of metal oxides. By taking advantage of the highly-exothermic reaction of Fe₂O₃ with Al, this study employed two thermite reagents, Al-Fe₂O₃ and Al-Fe₂O₃-SiO₂, blended with Fe and Si powders to serve as the reactant mixtures which were formulated to have a broad range of the starting composition. The effects of thermite mixtures and sample stoichiometries were investigated on the reaction exothermicity, combustion wave velocity and temperature, and phase compositions of the final products. In addition, the activation energy of the synthesis reaction was experimentally deduced from combustion wave kinetics.

2. Materials and Methods

The starting materials of this study included Fe_2O_3 (Alfa Aesar Co., Ward Hill, MA, USA, <45 µm, 99.5%), SiO₂ (Strem Chemicals, Newburyport, MA, USA, 99%), Al (Showa Chemical Co., Tokyo, Japan, <45 µm, 99.9%), Fe (Alfa Aesar Co., <45 µm, 99.5%), and Si (Strem Chemicals, <45 µm, 99.5%). Two thermite mixtures using Al as the reducing agent were prepared: one contains two oxidants at a molar proportion of Fe_2O_3 :SiO₂:Al = 0.6:0.6:2 and the other consists only of Fe_2O_3 and Al at a ratio of Fe_2O_3 :Al = 1:2. Reactions (1) and (2) expressed below represent two combustion systems formulated with different thermite reagents and adjustable amounts of elemental Fe and Si powders for the synthesis of FeSi-Al₂O₃ composites.

$$0.6Fe_2O_3 + 0.6SiO_2 + 2Al + (x - 1.2)Fe + (x - 0.6)Si \rightarrow xFeSi + Al_2O_3$$
(1)

$$Fe_2O_3 + 2Al + (y - 2)Fe + ySi \rightarrow yFeSi + Al_2O_3$$
 (2)

where stoichiometric coefficients *x* and *y* are related to the amounts of Fe and Si powders in the reactant mixture, and also signify the molar ratio of FeSi/Al₂O₃ formed in the final product. The metallothermic reaction of Fe₂O₃ + 2Al \rightarrow 2Fe + Al₂O₃ is extremely exothermic with T_{ad} = 3622 K, while exothermicity of aluminothermic reduction of SiO₂ (T_{ad} = 1760 K) is much weaker [24]. This suggests that Reaction (1) is less energetic than Reaction (2), since co-reduction of Fe₂O₃ and SiO₂ occurs in Reaction (1). Moreover, because FeSi has low formation exothermicity (T_{ad} = 1650 K), the increase of Fe and Si additions imposes a dilution effect on combustion. Accordingly, this study performed Reaction (1) with *x* varying from 1.2 to 2.5, within which stable and self-sustaining combustion was reached. It is apparent that the minimum value of *x* for Reaction (1) is 1.2, where no elemental Fe is added. When Reaction (1) was conducted with *x* > 2.5, it was found that, probably owing to inadequate reaction exothermicity, combustion was barely selfpropagating and the phase conversion was incomplete.

On account of the reaction exothermicity, Reaction (2) is more favorable for the formation of higher contents of FeSi in the product. Stable and self-sustaining combustion for Reaction (2) occurs in the range of $2.5 \le y \le 4.5$. For Reaction (2) with y = 2.0 (i.e., no addition of elemental Fe), violent combustion caused eruption of the reactants and massive melting of the sample, bringing about difficulty in recovering the end product. However, Reaction (2) with x > 4.5 appeared to be deficient in thermal energy to complete the phase conversion.

Calculation of T_{ad} was performed for Reactions (1) and (2) under different *x* and *y*, based on the following energy balance equation [25,26] with thermochemical data taken from [18,27].

$$\Delta H_r + \int_{298}^{T_{ad}} \sum n_j C_p(P_j) dT + \sum_{298 - T_{ad}} n_j L(P_j) = 0$$
(3)

where ΔH_r is the reaction enthalpy at 298 K, n_j is the stoichiometric constant, C_p and L are the heat capacity and latent heat, and P_j refers to the product.

The SHS experiment was conducted in a combustion chamber equipped with quartz viewing windows and filled with high-purity (99.99%) argon at 0.2 MPa. Reactant powders were well mixed in a ball mill, and then the mixture was uniaxially compressed in a stainless-steel mold at a pressure of 60–70 MPa to form cylindrical test specimens with 7 mm in diameter, 12 mm in height, and a relative density of 55%. The propagation velocity of combustion wave (V_f) was determined from the time series of recorded images. From the time derivative of combustion front trajectories, it was found the flame-front propagation velocity decelerated, finally reaching a nearly constant value. The relatively high propagation velocity in the beginning was attributed to the thermal energy supplied by the igniter. The constant velocity in the later stage represents the self-sustaining propagation of flame front and is reported in this study.

The thermocouple used in this study is R-type thermocouple (Omega Engineering Inc., Norwalk, CT, USA) with an alloy combination of Pt/Pt-13%Rh. The wire diameter is 62.5 μ m, bead size 125 μ m, and wire length 40 mm. The thermocouple bead was firmly attached on the sample surface at a position about 7 mm below the ignition plane. At this location, self-sustaining combustion was well developed, so that the measurement of combustion front temperature was justified. Details of the experimental setup were reported elsewhere [28]. Phase constituents of the final products were analyzed by X-ray diffraction (XRD) patterns from an X-ray diffractometer (Bruker D2 Phaser, Billerica, MA, USA) with CuK_{α} radiation.

The temperature dependence of combustion wave velocity offers a relationship to determine the activation energy (E_a) of the solid-state combustion reaction. The combustion wave velocity derived from an energy equation with a heat source can be expressed as [29,30]

$$V_f^2 = \frac{2\lambda}{\rho Q} \frac{RT_c^2}{E_a} k_o \exp(-E_a/RT_c)$$
(4)

where λ is the thermal conductivity, ρ the density, R the gas constant, Q the heat of reaction, T_c the combustion front temperature, and k_o the Arrhenius rate constant. Thus, E_a can be obtained from the slope of a best-fitted linear line correlating $\ln(V_f/T_c)^2$ with $1/T_c$ [30].

3. Results and Discussion

3.1. Thermodynamic Analysis

The calculated ΔH_r and T_{ad} of Reactions (1) and (2) under different stoichiometric coefficients are presented in Figure 1a,b, respectively. With the increase of *x* from 1.2 to 2.5 for Reaction (1), Figure 1a shows an increase in ΔH_r from -667.4 to -760.2 kJ, but a decrease in T_{ad} from 3355 to 2847 K. The increase of total reaction enthalpy is justified,

because both the aluminothermic reaction and formation of FeSi release heat. However, due to weak exothermicity of the FeSi formation, the value of T_{ad} decreases with increasing content of FeSi. For Reaction (2) with *y* increasing from 2.5 to 4.5, Figure 1b shows a rise in ΔH_r from -975.8 to -1118.6 kJ and a fall in T_{ad} from 3418 to 2872 K. Similar trends are observed for both reaction systems and Reaction (2) is more energetic than Reaction (1). At the same coefficients of *x* and *y* equal to 2.5, it can be seen that T_{ad} of Reaction (2) is higher than that of Reaction (1). Thermodynamic analysis confirms that both reaction systems are thermally satisfactory under the selected conditions. Because the calculated adiabatic temperatures are higher than the criterion proposed by Merzhanov [19], self-sustaining combustion can occur.





Besides thermodynamic considerations, the synthesis of FeSi-Al₂O₃ composite via autowave combustion with metallothermic reduction has to overcome the kinetic limitation of the reaction. Kinetic restraints are caused by incomplete reactivity owing to the presence of diffusion barriers. It is believed that the reduction of Fe₂O₃ by Al to produce Fe and Al₂O₃ acts as the initiation step, followed by aluminothermic reduction of SiO₂ in the case of Reaction (1). Subsequently, FeSi is produced through the interaction between Fe and Si.

3.2. Self-Sustaining Combustion Wave Kinetics

Figure 2a,b illustrate two typical combustion sequences observed in this study and are respectively recorded from Reaction (1) of x = 1.5 and Reaction (2) of y = 4.5. Firstly of all, Figure 2 confirms the establishment of self-propagating combustion for Reactions

(1) and (2). It is evident that for both SHS processes, a well-defined combustion front forms upon ignition and propagates along the sample compact in a self-sustaining manner. Secondly, Figure 2a,b signify different combustion behavior. As shown in Figure 2a, the flame propagation was fast and it took about 3.33 s for the combustion wave to traverse the sample. Moreover, combustion was in companion with obvious melting of the sample, suggestive of strong exothermicity of this test condition. On the other hand, Figure 2b exhibits a relatively slow combustion wave with a long spreading time of about 6 s and that the melting of the sample is considerably alleviated. Namely, a comparison between Figure 2a,b indicated that the increase of Fe and Si additions changed the combustion behavior from a rapid/molten mode to a moderate style and lowered the flame-front speed, due to a decrease in combustion exothermicity.



Figure 2. Self-propagating combustion sequences associated with formation of FeSi-Al₂O₃ composites: (a) Reaction (1) with x = 1.5 and (b) Reaction (2) with y = 4.5 (Unit of scale bar: 1 mm).

Figure 3 reveals the variations of flame-front propagation velocity (V_f) of Reactions (1) and (2) with their corresponding stoichiometric coefficients, *x* and *y*. A significant decline in the combustion wave speed from about 3.9 to 1.1 mm/s was observed for Reaction (1) with increasing *x* from 1.2 to 2.5. The decrease of combustion front velocity was ascribed to the dilution effect of Fe and Si additions, because the formation of FeSi was less energetic than aluminothermic reduction of oxide reagents. Similarly, the combustion velocity of Reaction (2) decreased from 4.5 mm/s at *y* = 2.5 to 1.5 mm/s at *y* = 4.5. The combustion propagation rate is mostly governed by the layer-by-layer heat transfer from the reaction zone to unburned region. Namely, the reaction zone temperature has a great influence on combustion wave velocity.



Figure 3. Effects of stoichiometric coefficients (*x* and *y*) on flame-front propagation velocities of Reactions (1) and (2).

Typical combustion temperature profiles measured from the samples of Reactions (1) and (2) are depicted in Figure 4. The profile features a sharp rise to the highest point, followed almost immediately by a considerable decline owing to heat losses to the surroundings. This implies a thin reaction zone. The sudden increase signifies the rapid arrival of the combustion wave. The peak value represents the combustion front temperature (T_c). A decrease in T_c with stoichiometric coefficient was detected for both reaction systems. Figure 4a indicates that T_c of Reaction (1) decreases from 1710 °C at x = 1.2 to 1413 °C at x = 2.5, confirming the dilution effect on combustion by increasing Fe and Si additions. Likewise, as shown in Figure 4b, the increase of y from 2.5 to 4.5 lowers the T_c of Reaction (2) from 1826 to 1506 °C. Due to the fact that the thermite mixture of Fe₂O₃ + 2Al is more exothermic than that of $0.6Fe_2O_3 + 0.6SiO_2 + 2Al$, the value of T_c of Reaction (2) is higher than that of Reaction (1) under the same stoichiometric coefficient of 2.5. Moreover, the dependence of combustion front temperature on sample stoichiometry is in a manner consistent with that of combustion wave velocity.

The accuracy of fine-wire thermocouple measurement is essentially affected by the conduction cooling and radiation loss. According to Bradley and Matthews [31], the conduction loss from the thermocouple depends on the length of wire between the junction and the support. The dimension of the thermocouple used in this study explains why the measurement was practically unaffected by the conduction cooling [31]. The radiation loss from the thermocouple bead is another major source of error in the thermocouple measurement. An estimate of the radiation correction was performed, assuming that a steady state existed between the convective heat transfer to, and radiation loss from, the thermocouple bead [32,33]. Radiation corrections for the combustion front temperatures measured in this study are in the range from 28 to 36 °C, which is more significant in the regions of higher temperatures. After the radiation correction, it is believed that the accuracy of the combustion temperature measurement is within ± 10 °C. When compared with the calculated T_{ad} , however, the measured T_c was much lower. This suggests that the burning samples experienced substantial heat losses to the surrounding gas by conduction and convection and to the chamber wall by radiation.



Figure 4. Variations of combustion temperature with stoichiometric coefficients (*x* and *y*): (**a**) Reaction (1) and (**b**) Reaction (2).

According to combustion wave kinetics [29,30], as mentioned above, the activation energy of solid-state combustion can be determined from the correlation between $\ln(V_f/T_c)^2$ and $1/T_c$. Figure 5 plots two sets of experimental data with their respective best-fitted linear lines. For Reaction (1), five data points from left to right were according calculated from V_f and T_c of x = 1.2, 1.5, 1.75, 2.0, and 2.5. Five data points of Reaction (2) from left to right are orderly associated with y = 2.5, 3.0, 3.5, 4.0, and 4.5. From the slopes of two straight lines, the values of $E_a = 215.3$ and 180.4 kJ/mol were deduced for Reactions (1) and (2), respectively. A smaller E_a for Reaction (2) means a lower kinetic barrier for the synthesis reaction to occur. Because the aluminothermic reduction is considered as the initiation step of the SHS process, co-reduction of Fe_2O_3 and SiO_2 by Al is probably responsible for the large E_a obtained for Reaction (1). When compared with $E_a = 145 \text{ kJ/mol}$ reported for the Al-Fe₂O₃ thermite reaction [34], Reactions (1) and (2) of this study have higher kinetic barriers to conquer. This could be most likely caused by the fact that in addition to aluminothermic reduction, Reactions (1) and (2) involve chemical interactions between Fe and Si to form FeSi. These interactions could be complex and occur in both sequential and parallel manners during the SHS process.



Figure 5. Correlation of V_f and T_c for determination of activation energies (E_a) of Reactions (1) and (2).

3.3. Phase Constituents of Synthesized Products

Figure 6a–c presents the XRD patterns of SHS-produced composites from Reaction (1) with x = 1.2, 1.5, and 2.0, respectively. Formation of FeSi (ICSD card number: 88-1298) and Al₂O₃ (ICSD card number: 88-0826) with almost no other phases was achieved, suggesting that both the aluminothermic reduction and chemical interaction were complete for Reaction (1). The intensity of the signature peaks of FeSi is obviously stronger in Figure 6c than Figures 6a and 6b. This confirms an increase in the ratio of FeSi/Al₂O₃ in the end product. The weak peaks between the signals of main phases in Figure 6 might reflect the presence of a tiny amount of impurities. The impurity phase possibly existing in the final products is considered to be aluminum silicate (or called mullite). Mullite is a stable solid solution compound in the Al₂O₃-SiO₂ system. The stoichiometry of mullite refers to Al_{4+2m}Si_{2-2m}O_{10-m} with *m* varying between about 0.2 and 0.9 and the composition ranges from relatively silica-rich 3Al₂O₃·SiO₂ (3:2 mullite) to alumina-rich 2Al₂O₃·SiO₂ (2:1 mullite) [35]. Formation of aluminum silicate was attributable to dissolution of a small amount of Si into Al₂O₃ during the SHS process. To be shown below in Figure 7, the signature peaks of aluminum silicate are detectable, because the amount of Si is increased in the sample.



Figure 6. XRD patterns of FeSi-Al₂O₃ composites synthesized from Reaction (1) with (**a**) x = 1.2, (**b**) x = 1.5, and (**c**) x = 2.0.



Figure 7. XRD patterns of FeSi-Al₂O₃ composites synthesized from Reaction (2) with (a) y = 2.5, (b) y = 3.5, and (c) y = 4.0.

The XRD spectra of the final products synthesized from Reaction (2) with y = 2.5, 3.5, and 4.0 are shown in Figure 7a–c. Both FeSi and Al₂O₃ were identified and the peak intensity of FeSi relative to Al₂O₃ was augmented in the case of y = 4.0 when compared to those of y = 2.5 and 3.5. Besides, as indicated in Figure 7, aluminum silicate was detected in the final products. As can be seen in Figure 7, the quantity of aluminum silicate slightly increased with increasing FeSi content formed in the product, because the sample contained more Si.

4. Conclusions

The SHS process involving metallothermic reduction of Fe_2O_3 and SiO_2 by Al and the elemental reaction of Fe with Si was conducted to fabricate FeSi-Al₂O₃ composites with a broad composition range. Thermite reagents made up of $0.6Fe_2O_3 + 0.6SiO_2 +$ 2Al and Fe_2O_3 + 2Al were incorporated into the Fe-Si reaction system. Aluminothermic reduction of metal oxides generated Al₂O₃ and released a large amount of the reaction enthalpy which was adequate to sustain the combustion reaction in a self-propagating manner. The SHS reaction including the mixture of $0.6Fe_2O_3 + 0.6SiO_2 + 2Al$ was less exothermic than that containing the reagent of $Fe_2O_3 + 2AI$. Moreover, the increase of Fe and Si additions for the production of a higher content of FeSi reduced the overall reaction exothermicity. Consequently, the former was adopted to produce the composites with a molar ratio of $FeSi/Al_2O_3$ from 1.2 to 2.5, within which a decrease in both the combustion wave velocity from 3.9 to 1.1 mm/s and reaction front temperature from 1710 to 1413 °C was observed. The latter was applied to fabricate the composites with $FeSi/Al_2O_3$ from 2.5 to 4.5; within this range, the increase of $FeSi/Al_2O_3$ lowered the reaction temperature from 1826 to 1506 °C and decelerated the combustion wave from 4.5 to 1.5 mm/s. Correlation of combustion wave kinetics indicated that the SHS reaction based on $0.6Fe_2O_3 + 0.6SiO_2$ + 2Al had a larger E_a of 215.3 kJ/mol in comparison to $E_a = 180.4$ kJ/mol for the reaction constructed out of $Fe_2O_3 + 2Al$. The difference in E_a could be ascribed to co-reduction of Fe_2O_3 and SiO_2 by Al, in contrast to the sole reduction of Fe_2O_3 . The formation of FeSi and Al₂O₃ in the final products was identified by XRD analysis. The increase of the FeSi content with increasing Fe and Si additions was confirmed. Phase conversion from the reactants to products was completely achieved, except for a trivial amount of aluminum silicate present in the end products with a high FeSi content.

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