Preparation of Fe₂AlB₂ material via thermal explosion induced by spark plasma sintering

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ABSTRACT

Fe₅AlB₂ material was prepared through spark plasma sintering (SPS) by using Fe/Al/B mixed powder as the raw material. The effects of sintering temperature, holding time, and Al content on the phase composition and microstructure of the product were studied to obtain materials with high Fe₅AlB₂ content. Results showed that when the sintering temperature was increased to approximately 1000°C, SPS induced a thermal explosion reaction, resulting in the formation of a dense sintered sample with high Fe₅AlB₂ content. The sample contained a small amount of FeB and Fe₃Al₄ impurities. The synthesis of Fe₅AlB₂ could be promoted by optimizing holding time and increasing Al content in the raw materials. The most suitable process parameters for the synthesis of materials with high Fe₅AlB₂ content were 1000°C, no holding, and 2Fe/1Al/28 raw material. The Fe₅AlB₂ sample had good mechanical properties. Its Vickers hardness and bending strength were 10.5 GPa and 352 MPa, respectively. Given that the synthesized Fe₅AlB₂ material was unstable, continuously increasing the temperature or extending the holding time would cause it to decompose.

1. Introduction

Several studies [1,2] have recently shown that main group (IIIA and IVA group) elements can be introduced into binary borides to improve their high hardness and brittleness. The resulting transition-metal ternary borides are called MAB phase ceramic materials, in which M is a transition metal, A is mainly IIIA and IVA group elements, and B is the boron element. The MAB phase ceramics that have been reported thus far mainly include MoAlB [3], Cr₂AlB₂ [4], Cr₃AlB₃ [5], Fe₅AlB₂ [6], and Mn₃AlB₂ [7]. These materials show many excellent properties of metals and ceramics, including good conductivity, thermal conductivity, and fracture toughness and excellent resistance against high-temperature oxidation. Fe₅AlB₂ is an important member of MAB phase ceramics. In 2013, Fe₅AlB₂ was found to exert a large magnetocaloric effect in magnetic refrigeration, and its Curie temperature is approximately 300 K near room temperature [8,9]. Therefore, it has considerable practical value in becoming a new high-temperature structural ceramic and magnetic refrigeration material.

Although the preparation of materials is the basis of experimental research, reports on Fe₂AlB₂ are scarce. Arc melting [8,9], furnace spinning [10], pressure-less sintering [11], and hot pressing sintering [12] have been used in recent years to prepare Fe₂AlB₂. For example, in 2013, Tan et al [8] obtained Fe₂AlB₂ crystals via arc melting. Fe₂AlB₂ materials with high purity were obtained through 7 days of annealing at 900°C and subsequent treatment with diluted HCl solution for 10 min. In 2016, Barsoum et al [11]. heated FeB and Al powder raw materials in a tubular furnace with H₂ protection to 1000°C for 15 h. Fe₂AlB₂ powders containing a small amount of Al₂O₃ impurities were obtained after half an hour of dilute HCl solution treatment. In 2016, Fe₂AlB₂ bulk with high content was prepared through hot pressing sintering at 1100°C for 1 h with FeB and Al powders as raw materials [12].

Spark plasma sintering (SPS) technology is an advanced sintering technology wherein the pulse current heating method is used. It has the characteristics of relatively uniform heating, short sintering time, and fast heating speed [13]. At present, high-content MoAlB ceramic bulks have been prepared through SPS technology [14]. However, reports on Fe₂AlB₂ materials prepared through SPS do not exist.

In this work, Fe, Al, and B powders were used as raw materials to synthesize Fe₂AlB₂. The effects of sintering temperature, holding time, and raw material ratio on the phase composition and microstructure of the sample prepared via SPS were studied.
2. Experimental procedure

The experimental materials were Fe powder purchased from the market (purity > 99.0%, average particle size of 53 μm), Al powder (purity > 99.0%, average particle size of 53 μm), and B powder (purity > 99.0%, average particle size of 2 μm). The raw materials were mixed in accordance with the material ratio of 2Fe/XAl/2B (X = 1, 1.05, 1.1, 1.2). The mixed powder was placed into a graphite mold with an inner diameter of 30 mm and then sintered in a SPS machine. The sintering temperature was 900°C–1200°C, and the heating speed was 100°C/min. The temperature was held for different durations. The pressure was 30 MPa. Cooling was performed in the furnace at the heating speed of 100–200°C/min.

The 2Fe/Al/2B mixed powder was pressed into a green body with a diameter of 10 mm and a thickness of approximately 5 mm through a molding process at a pressure of 100 MPa. The pressed body was placed into a TTI-type rapid heating furnace. The heating rate was 40°C/min, the heating temperature was 800°C, and the heat preservation was 1 min.

The phase analysis of the synthesized powder was conducted with a RIGAKU Ultima IV (CuKα radiation) rotating target X-ray polycrystalline diffractometer (XRD). The microstructure of the material was analyzed by applying a field-emission scanning electron microscope. The relative density, four-point bending flexural strength, and hardness (Vickers indentation, 10 Kgf) of the samples were measured by using a solid density meter (MH-300), a universal testing device, and a Vickers hardness tester (HV50A), respectively. Differential scanning calorimetry (DSC) were conducted under flowing Ar atmosphere using thermal analysis (STA-449-F3, Netzsch) at a heating rate of 10°C/min.

3. Results and discussion

Figure 1 shows the XRD patterns of the 2Fe/1Al/2B mixed powders sintered at different temperatures without heat preservation. As shown in Figure 1, the sample sintered at 950°C was composed of Fe, FeAl<sub>x</sub>, Fe<sub>0.6</sub>A1<sub>0.6</sub>, Al<sub>1.3</sub>Fe<sub>x</sub>, and FeB. Obviously, no thermal explosion reaction occurred at 950°C. The sample sintered at 1000°C had a main phase of Fe<sub>2</sub>AlB<sub>2</sub> and contained a small amount of impurities, such as FeB and FeAl<sub>3</sub>. This result indicated that a thermal explosion reaction occurred during the heating process. The reaction most likely occurred at approximately 1000°C, and Fe<sub>2</sub>AlB<sub>2</sub>, FeAl<sub>3</sub>, and FeB were formed.

When the temperature was further increased to 1100°C, the phase composition of the sample basically remained unchanged. However, when the temperature was elevated to 1200°C, the main phase of the sample transformed into FeB, and the relative diffraction peak intensity of Fe<sub>2</sub>AlB<sub>2</sub> became considerably weaker. Fe<sub>2</sub>AlB<sub>2</sub> underwent serious decomposition at 1200°C, resulting in the formation of FeB and Al [15,16]. Given that Al easily volatilized into the environment at high temperatures, it could not be observed in the XRD patterns of the products.

Figure 2 shows the fracture morphology of the 2Fe/1Al/2B mixed powders sintered at different temperatures. As can be seen from Figure 2 (a), (b), the microstructure of the sample was relatively loose, and the size and morphology of the structure were not uniform. Increasing the temperature to 1000°C–1100°C resulted in a sample with dense microstructure. Terraced Fe<sub>2</sub>AlB<sub>2</sub> grains (identified by using XRD and EDS (Figure 3)) were obtained. Notably, the porosity of the sample increased slightly at 1100°C, the sample sintered at 1200°C was mainly composed of equiaxed FeB grains as confirmed via XRD and EDS. The morphology of terraced Fe<sub>2</sub>AlB<sub>2</sub> grains was difficult to observe.

Thermal explosion reaction is a combustion reaction [17] suitable for the synthesis of intermetallic compounds with low heat release. The compact powder was first placed into the heating furnace and heated evenly at a certain heating rate. When the ignition temperature was reached, the combustion reaction suddenly occurred in the whole compact. Like an “explosion,” the large amount of heat released by the reaction resulted in the sharp increase of temperature, thereby reaching the maximum temperature (adiabatic temperature). Finally, the synthesis reaction was completed in an instant.

In the process of spark plasma sintering heating, thermal runaway occurs when the joule heating of the sample exceeds the radiation heating from the die and becomes the main input energy [18,19]. This thermal runaway may induce a thermal explosion.
reaction. Sudden thermal change can show a sudden change of pulse current or voltage in the process. In a previous work on SPS-induced thermal explosion reaction of the Mg-Si [20] and Ti-Si-C systems [21], pulse current mutation and the corresponding thermal explosion reaction also occurred.

Figure 4 shows a schematic diagram of the change of current with temperature during the heating of 2Fe/1Al/2B sample by SPS. Figure 4 shows that the pulse current increased linearly with increasing temperature. However, a small peak appeared at 976°C. This result showed that at approximately 976°C, a sudden chemical reaction occurred, and this reaction was completed in a very short time. Therefore, we speculated that a thermal explosion reaction occurred at this temperature point.

The DSC result of 2Fe/1Al/2B sample in Figure 5 shows that the reaction with low exothermic heat occurred at 971.2°C.

Figure 6 shows (a) XRD and (b) SEM of 2Fe/1Al/2B sample after SPS treatment at 980°C. Figure 6(a) shows that the main phase of the product was Fe$_2$AlB$_{2}$ material. The sample was composed of many stepped Fe$_2$AlB$_{2}$ grains, and many pores with sizes in the range of 1–2 μm were present. Considering that the time of thermal explosion reaction was very short, and no heat preservation treatment was performed, many pores easily formed.

The above XRD and SEM results showed that the 2Fe/1Al/2B powder might undergo thermal explosion at approximately 976°C and produce high Fe$_2$AlB$_{2}$
sintered at 1100°C had increased, the most suitable temperature for the synthesis and sintering densification of Fe$_2$AlB$_2$ was 1000°C. On the basis of the above analysis, 1000°C was used as the sintering temperature in the following research.

Considering that Al might volatilize during sintering, the synthesis of Fe$_2$AlB$_2$ could be promoted by increasing the Al content of the raw materials. Figure 7 shows the XRD spectrum of the sample fabricated with 2Fe/XAl ($X = 1, 1.05, 1.1, 1.2$)/2B mixed powder sintered at 1000°C without holding. As can be observed in Figure 7, the synthesis of Fe$_2$AlB$_2$ could be promoted by increasing the Al content of the raw material ($X = 1.1$). The main phase of the product was Fe$_2$AlB$_2$, and the diffraction peak of the impurity phases was very weak. Further increasing Al content would lead to a significant enhancement in the diffraction peak of FeB.

Considering that some impurity phases remained in the product, holding time was further increased to promote the complete elimination of the impurity phases. Figure 8 provides the XRD spectra of the samples obtained by sintering 2Fe/1.1Al/2B mixed powders at 1000°C with different holding times. As can be observed in Figure 8, the diffraction peak of FeB in the product increased slightly when the holding time was extended for only 15s. With the prolongation of the holding time, the diffraction peak of FeB in the sample increased gradually, and a weak Fe$_2$B diffraction peak appeared. When the holding time was 3 min, the diffraction peak of FeB in the sample strengthened.

Figure 9 shows the fracture SEM of the sample synthesized with 2Fe/1.1Al/2B mixed powders sintered at 1000°C without holding. It was similar to that of the sample fabricated from 2Fe/1Al/2B mixed powder (Figure 2(c,d)) and was also composed of a large number of Fe$_2$AlB$_2$. At the same time, the number of pores in the sample was very small.

The results provided in Figure 1 and Figure 8 show that the decomposition of Fe$_2$AlB$_2$ was induced by increasing the temperature or holding time after the synthesis of high-content Fe$_2$AlB$_2$ material. The results indicated that Fe$_2$AlB$_2$ began to decompose violently at 1200°C.

In accordance with the literature [15,16], Fe$_2$AlB$_2$ decomposed at temperatures above 1237°C under the protection of Ar. The decomposition products were FeB and Al.

$$\text{Fe}_2\text{AlB}_2 \rightarrow 2 \text{FeB} + \text{Al} \quad (1)$$

The volatilization of Al increased the porosity of the product. The thermal stability of Fe$_2$AlB$_2$ in the SPS environment in this work was lower than that in previous studies [15,16] mainly because at the moment of discharge, the microzones of the sample could produce a high temperature that was higher than the temperature measurable by the infrared pyrometer.
Therefore, FeB was expected to form more easily than Fe$_3$B in the reaction. The $\Delta G$ values of the Fe–Al compounds reached zero at approximately 1100 K–1200 K, indicating that these reactions would not be spontaneous above this temperature.

Merzhanov thought that systems with adiabatic temperature $>1800$ K can become self-sustaining [17]. That is, the reaction can maintain itself after it is initiated. Given the lack of thermodynamic research on Fe$_2$AlB$_2$ materials, calculating the adiabatic temperature and enthalpy change of Fe$_2$AlB$_2$ materials produced via the reaction of the Fe–Al–B system is impossible. The adiabatic temperature of the reaction system can be roughly assumed to be 1800 K. As inferred from Figure 10, at temperatures below 1800 K, almost all the materials of the Fe–Al–B system might decompose and melt or the reaction could not be spontaneous. Only FeB was very stable at temperatures above 1800 K. Figure 10 illustrates that FeB was the main impurity phase in the above sintered products.

A green body was prepared, and the thermal explosion reaction was carried out in a tubular furnace to further study the mechanism of the thermal explosion of 2Fe/1Al/2B mixed powders.

Figure 11 shows the appearance of (a) the green body and (b) the reacted product obtained through the thermal explosion of 2Fe/1Al/2B powders in a tube furnace. Figure 11 (b) reveals that the green body turned into a powder after thermal explosion. Generally, after thermal explosion, the green body became a hard porous sintered body. This phenomenon fully indicated that the exothermic heat of the reaction and the adiabatic temperature were insufficiently high. These common factors led to the ineffective sintering of the green body. In addition, many spherical metal or alloy particles (indicated by the arrow) were present in the powder. These particles should be melted particles formed by Al melting or the Fe–Al eutectic.

Figure 12 shows the XRD pattern of the hot explosion products of the 2Fe/1Al/2B powder compacts in a tubular furnace. Figure 12 shows that some of the raw materials had been reacted into FeAl, Fe$_3$Al, FeB, Fe$_2$B, AlB$_2$, and Fe$_2$AlB$_2$. As a result of their detonation into powder, many raw materials were incompletely reacted.

The thermal explosion phenomenon in the tube furnace can provide considerable information.

(1) The results provided in Figure 11 and Figure 12 were consistent with the DSC results given in Figure 5. That is, the heat released and the adiabatic temperature of the reaction of 2Fe/1Al/2B powder into Fe$_2$AlB$_2$ were low. Meanwhile, the Fe–Al powders showed antidensification
behavior during sintering. These factors prevented the easy sintering of the product. Instead, the product was detonated into powder. (2) This can be assumed to be similar to the quenching treatment in the process of thermal explosion. As inferred from this result, many intermediate products, such as FeAl and FeB, formed after thermal explosion. These phases will react with each other to form Fe$_2$AlB$_2$. This result also validated the thermodynamic analysis illustrated in Figure 10.

In the SPS environment, plasma can increase the temperature of the microregion of the sample, and axial pressure can also induce the raw materials to come into full contact, thus inhibiting the antidensification behavior of Fe–Al powders. Finally, Fe$_2$AlB$_2$ with high content could be obtained.

On the basis of the above study, the possible kinetic reaction path of the Fe$_2$AlB$_2$ material prepared through the thermal explosion reaction was analyzed and discussed as follows:

An important reaction path was the solid–liquid reaction mechanism, that is, the reaction between FeB and liquid Al resulted in direct transformation into Fe$_2$AlB$_2$. The reaction equation is as follows:

$$2\text{FeB} + \text{Al} = \text{Fe}_2\text{AlB}_2$$ (2)

The initial temperature of thermal explosion was approximately 971°C, which was considerably higher than the melting point of Al. Therefore, in the process of thermal explosion, Al was in a liquid state. This solid–liquid reaction contributed to the rapid synthesis of Fe$_2$AlB$_2$. This reaction path has been demonstrated in the preparation of MAB phase materials, such as Fe$_2$AlB$_2$, MoAlB, and Cr$_2$AlB$_2$, through hot pressing sintering [2]. It has the advantages of simplicity and few impurities over other possible reaction systems. It leads to significantly reduced sintering temperatures and holding times.

Other reaction paths to the formation of Fe$_2$AlB$_2$ material were involved the three-phase reaction. The equations of these possible reaction paths are given below:

$$10\text{FeB}(s) + \text{AlB}_2(s) + \text{Fe}_2\text{Al}_5(s) = 6\text{Fe}_2\text{AlB}_2(s),$$ (3)

$$\text{FeB}(s) + \text{FeAl}(s) + \text{B}(s) = \text{Fe}_2\text{AlB}_2(s),$$ (4)

$$\text{Fe}_2\text{B}(s) + \text{Al}(l) + \text{B}(s) = \text{Fe}_2\text{AlB}_2(s),$$ (5)

$$2\text{Fe}_3\text{Al}(s) + \text{Al}(l) + 6\text{B}(s) = 3\text{Fe}_2\text{AlB}_2(s)$$ (6)

A disadvantage of these reaction paths is the presence of many kinds of reactants. This disadvantage often results in increased reaction temperatures and holding time. However, their products contain very few impurities, such as FeAl$_x$ and AlB$_2$.

Although many reaction paths for the synthesis of Fe$_2$AlB$_2$ exist, one of the characteristics of thermal explosion is that its reaction time is brief (only approximately 1–2 s). In the SPS experiment, the cooling rate reached 100–200°C/min. Therefore, from the kinetics point of view, the main reaction path suitable for the synthesis of Fe$_2$AlB$_2$ material must be the one resulting

![Figure 9](image-url) The fracture SEM images of 2Fe/1.1Al/2B mixed powders sintered at 1000°C without holding time.

![Figure 10](image-url) Change of Gibbs free energy (ΔG) as function of temperature for reactions among Fe-Al-B system.
FeB by-products was produced. If an ordinary solid-state reaction was adopted, then a large number of impurities, such as FeB, Fe₃B, and FeAlₓ, will be formed. This will greatly prolong the time required to synthesize a high content of Fe₂AlB₂ materials and will inevitably produce many kinds of impurities at high content.

The mechanical properties of the Fe₂AlB₂ sample from 2Fe/1Al/B powders sintered at 1000°C without holding were tested. Similar to the mechanical properties of a previously reported Fe₂AlB₂ material [11,12], the Vickers hardness and bending strength of this material were 10.5 GPa and 352 MPa, respectively. In contrast to that in previous works [11,12], in this work, the rapid synthesis and densification of Fe₂AlB₂ materials at low temperatures were realized via thermal explosion induced by SPS in the Fe–Al–B system.

4. Conclusion

The thermal explosion of the Fe–Al–B system was induced by using SPS technology. Dense materials with high Fe₂AlB₂ content could be obtained by adjusting the heating temperature, holding time, and raw material ratio. A dense sintered body with high Fe₂AlB₂ content was successfully prepared from 2Fe/1.1Al/B mixed powders at 1000°C without holding. The Fe₂AlB₂ phase present in the product was terraced with well-developed grains. The material had good mechanical properties. Its Vickers hardness was 10.5 GPa, and its bending strength was 352 MPa.

Disclosure statement

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