Combustion Synthesis of TiC–Fe Composites under the Action of an Electric Field

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Using thermal simulation equipment, the combustion synthesis process of the compact of 55wt%(Ti+C)–45wt%Fe was studied. The results show that the ignition temperature of Fe–Ti–C system can be decreased greatly under the action of electric field and great thermal density. Before heating up to 350°C, although there is no reaction takes place in the system, the microstructure of the system changes with the temperature; During heating from 350–470°C, a thermal explosion phenomenon appears. Especially in the earlier stage of the combustion reaction, the dominant reaction is the one synthesized TiC; As the temperature up to 670°C continuously, $Ti_{(s)} + C_{(s)} = TiC_{(s)}$ reaction takes place accompanying with $2Fe_{(s)} + Ti_{(s)} = Fe_2Ti_{(s)}$, and the conversion degrees of these reactions are increasing with the temperature increasing gradually. However, a part of Fe_2Ti will be decomposed with the temperature increasing further, as a result, $Ti_{(s)} + C_{(s)} = TiC_{(s)}$ will go on because of the addition Ti. Consequently, the synthesized product consist of Fe, TiC and a little of Fe_2Ti , and ultrafine TiC particles distribute in the Fe matrix uniformly.

KEY WORDS: combustion synthesis; electric field; Fe–Ti–C system.

1. Introduction

As a materials synthesis technology development rapidly in last decade or so, combustion synthesis (CS) has been successfully applying in the synthesis of high temperature refractory materials such as ceramic, metal-ceramic composition and intermetallics.^{1–3)} Those fields such as electric, magnetic and micro-gravity activated CS can be put into effective use in the system which is difficult to occur or react incompletely under normal condition, so it has been one of the important research aspects.^{4–6)}

The research group led by Z. A. Munir is a typical representation of electric field activated CS, they have synthesized many kinds of materials by this method and carried out a quality of research.^{5,6)} However, the electric field is put into use only when the system is ignited by outside ignited equipment in their research, in other word, electric field play the roles just in maintaining and controlling the process of combustion synthesis. Different from their method, the outside ignited equipment isn't needed in our research, and an electric field play the roles not only in maintaining and controlling the process of combustion, but also in promoting diffusion process among the reactant atoms at low temperature in order to reduce the starting temperature of reaction.^{7,8)}

TiC–Fe composites which can be used as cutting, machining and wear resistance materials draw much attention because of their extremely high hardness and toughness attributes. Although there are a few reports about the com-

bustion synthesis of TiC–Fe composites from Ti, C and Fe powders, all of them are based on conventional combustion synthesis.^{9–11)} The adiabatic temperature (T_{ad}) of Fe–Ti–C system decreases with the increasing of Fe content, accompanying Fe–Ti–C system changes from strong exothermic to weak exothermic system, and the conventional CS can't be realized when Fe content is more than 60 wt%.^{9,10)} Moreover, the conventional CS need high ignition temperature, and the lowest ignition temperature of Fe–Ti–C system is 1 060°C in all reported literatures.¹¹⁾ As a result, TiC particles in produce are liable to grow up, which make against the quality of this composite.

According to the previous research results, the ignition temperature of system can be decreased greatly under the action of electric field and great thermal density.^{7,8)} In order to overcome the shortcoming of conventional CS, electric field activated CS is a effective method of preparing high quality composites. At present, there is none of report about electric field activated the system of Fe–Ti–C combustion synthesis except for our research group. In this paper, the process of combustion synthesis of 55wt%(Ti+C)–45wt%Fe system with $T_{ad}=2\ 000\ K$ ³⁾ under the action of an electric field was studied.

2. Experimental

Powders of titanium, graphite and iron, all of them with a 99% purity, and the typical average size of $\sim 60\ \mu m$, were mixed thoroughly with 55wt%(Ti+C)–45wt%Fe (Ti/C

Fig. 1. Schematic representation of Gleeble equipment.

molar ratio of 1 : 1) using a ball mill for 6 h. Then the mixed powders were compressed in a steel-mould to form a green compact with diameter 12.8 mm, height 13.6 mm and relative density of 73 %.

Figure 1 shows the schematic of Gleeble thermal simulation equipment used in the experiments. It controls heating route and collects temperature data of a sample automatically by a computer system. Moreover, the character of this electric field is low voltage and large current.

In the experiment, no sooner had a series of same green compact been heated individually up to 250°C, 350°C, 470°C, 670°C and 800°C at preset heating rate of 600°C/s in vacuum ($<10^{-4}$ Pa) by the large electric current ($\sim 16\,500$ A) passing through them than the power was turned off. Meanwhile, the actual temperature data of the compact during the experiment were recorded at a frequency of 20 Hz. Finally, the components of synthesized products were identified by XRD, and microstructures were acquired by a metalloscope and SEM.

It should be mentioned that the selection of heating temperature is according to the results of the thermal analysis and high-temperature XRD of this system. Moreover, the fact of that the temperature distribution within the sample during the whole heating process is rather uniform was proved by previous test, for example, the maximum difference in temperature which is between the surface and centre of sample is just only 3–5°C, so in this experiment only the surface temperature was tested conveniently.

3. Results and Discussion

3.1. Products Characteristic

The XRD of the products of the samples under different heating temperatures are shown in Fig. 2. From Fig. 2 it can be seen that: the final component of samples heated up to 250°C, 350°C both consist of Fe, Ti and C, which indicate that there is no reaction occur in the system before heating up to 350°C; the products of the sample heated up to 470°C consist of new phase—TiC besides Fe, Ti and C, which demonstrates that there is an uncompleted reaction $\text{Ti}_{(s)} + \text{C}_{(s)} = \text{TiC}_{(s)}$ in the system before heating up to 470°C; the products of the sample heated up to 670°C consist of new phase— Fe_2Ti besides Fe, C, TiC without Ti, which indicates that $\text{Ti}_{(s)} + \text{C}_{(s)} = \text{TiC}_{(s)}$ reaction takes place accompanying with $2\text{Fe}_{(s)} + \text{Ti}_{(s)} = \text{Fe}_2\text{Ti}_{(s)}$ reaction, and reactant Ti is almost run out during this period; and the products of the sample heated up to 800°C consist of Fe, TiC and a little of

Fig. 2. X-ray diffraction patterns of synthesized products.

Fe_2Ti , which is similar to the conventional CS,^{9–11)} and it indicates that a part of Fe_2Ti will be decomposed so as to change into TiC.

As shown in Fig. 3, although there is no reaction occur in the system heated up to 250°C and 350°C, the microstructure of system has been changed to some degree, it can be seen that the interface between reactant particles of the compact heated up to 350°C is clearer than that one heated up to 250°C. And then, from Fig. 4 showed the SEM photos of samples heated up to 470°C, 670°C and 800°C, it can be seen that there are a great deal of 300–800 nm grey spherical particles which were identified as TiC by EDS

(a) 250°C

(b) 350 °C

Fig. 3. The metallographic photos of samples of heating temperature 250, 350°C.

distribute in Fe matrix uniformly. Moreover, the average size of TiC particles become larger associated with the heating temperature increasing.

3.2. The Thermodynamical Analysis of Fe–Ti–C System

The reactions in Fe–Ti–C system almost occur in state of solid when Fe content is above 40 wt%.^{3,12)} The phases which may be exist in this system under 800°C and the accompanying free energy changes that are calculated thermodynamically in this process condition are as follows¹³⁾:

$$\Delta G_1 = -182\,875 + 10.0738T \quad \text{J/mol} \dots\dots\dots(1)$$

$$\Delta G_2 = 26\,668.4 - 24.7456T \quad \text{J/mol} \dots\dots\dots(2)$$

$$\Delta G_3 = -87\,860 + 89.00T \quad \text{J/mol} \dots\dots\dots(3)$$

Where ΔG is free energy change.

Figure 5 describes the free energy changes of the above reactions. Based on these equations and Fig. 5, it can be seen that the ΔG values of Eq. (1) is negative except that of Eq. (2) is positive below 800°C, and that of Eq. (3) is negative just below 714°C and larger than that of Eq. (1). As a result, it reveals thermodynamically that the chemical reaction of $\text{Ti}_{(\text{s})} + \text{C}_{(\text{s})} = \text{TiC}_{(\text{s})}$ can take place below 800°C, and TiC is the most stable phase in the system. On the contrary, the chemical reaction of $3\text{Fe}_{(\text{s})} + \text{C}_{(\text{s})} = \text{Fe}_3\text{C}_{(\text{s})}$ can't take

(a) 470°C

(b) 670°C

(c) 800°C

Fig. 4. SEM photos of samples of heating temperature 470, 670, 800°C.

Fig. 5. The ΔG of equations as function of temperature in the system of Fe–Ti–C.

place below 800°C. However, the chemical reaction of $2\text{Fe}_{(\text{s})} + \text{Ti}_{(\text{s})} = \text{Fe}_2\text{Ti}_{(\text{s})}$ can take place below 714°C, but Fe_2Ti will be decomposed above 714°C. It is said that Fe_2Ti is the non-equilibrium transition phase of the non-equilibrium process-CS.

3.3. The Process of Combustion Synthesis of Fe–Ti–C System

In the condition of an electric field, the large electric current acquired by presetting heat rate up to 600°C/s can provide larger thermal density for Fe–Ti–C system. And then the common roles of electric and thermal field can provide the great contribution for the solid diffusion among reactant atoms at low temperature. For example, in Fig. 4(c), the EDS results which show that grey particle consist of 7.12 at% Fe, 74.24 at% Ti and 18.64 at% C and white area consist of 84.39 at% Fe, 3.79 at% Ti and 11.82 at% C demonstrate that not only C and Fe diffuse into Ti, but C and Ti also diffuse into Fe in the process of combustion synthesis of Fe–Ti–C system. In the same temperature, the rate of interstitial diffusion is higher than that of substitutional diffusion.¹⁴⁾ Diffusion of C into Ti and Fe occur by the interstitial diffusion, but the diffusion of Ti into Fe or Fe into Ti occurs by substitutional diffusion. So it can be suggested that the diffusion rate of C into Ti and Fe is higher than that of Ti into Fe or Fe into Ti, and the process of Ti into Fe or Fe into Ti may control the combustion synthesis process.

First, during the period of heating up to 350°C, although both $\text{Ti}_{(s)} + \text{C}_{(s)} = \text{TiC}_{(s)}$ and $2\text{Fe}_{(s)} + \text{Ti}_{(s)} = \text{Fe}_2\text{Ti}_{(s)}$ reactions can occur according to the above thermodynamical analysis, there is no reaction takes place in the system because of deficient energy in so low temperature. However, both the solid diffusion of C, Fe into Ti and C, Ti into Fe are strengthened by the common effect of electric field and large thermal density, and the transport properties such as electric conductivity, thermal conductivity change with the temperature. As a result, the microstructure of system changes with the increasing of the temperature. Second, with the heating temperature ranges from 350–470°C, the energy provided by the electric field for the system is rising gradually. When it is high enough to be ignited, a combustion phenomenon appears instantly throughout the entire sample which is named thermal explosion at the ignition temperature (the ignition temperature of this system is 394°C, as reported in Ref. 7)). In the earlier stage of the combustion reaction, the dominant reaction is the one synthesized TiC because $\text{Ti}_{(s)} + \text{C}_{(s)} = \text{TiC}_{(s)}$ reaction takes place more easily than $2\text{Fe}_{(s)} + \text{Ti}_{(s)} = \text{Fe}_2\text{Ti}_{(s)}$ reaction. Third, as the temperature increases continuously from 470–670°C, $\text{Ti}_{(s)} + \text{C}_{(s)} = \text{TiC}_{(s)}$ reaction takes place accompanying with $2\text{Fe}_{(s)} + \text{Ti}_{(s)} = \text{Fe}_2\text{Ti}_{(s)}$ reaction, and the degrees of conversion for these reactions are increasing gradually. Finally, when the temperature increases further, a part of Fe_2Ti will be decomposed to Fe and Ti, and then the addition Ti can react with the residual C until the temperature rises to the preset highest temperature 800°C. Consequently, the syn-

thesized products consist of Fe, TiC and a little of Fe_2Ti which is the transition phase of non-equilibrium process.

4. Conclusions

The ignited temperature of Fe–Ti–C system can be reduced greatly by the common roles of electric field and large thermal density.

The process of the electric field induced combustion synthesis can be described as follow: Before heating up to 350°C, the solid diffusion among reactant atoms is strengthened gradually by the common effect of electric field and large thermal density with the temperature increasing. Although there is no reaction takes place in the system, the microstructure of system changes with the temperature; During heating from 350–470°C, a thermal explosion phenomenon appears. Especially in the earlier stage of the combustion reaction, the dominant reaction is the one synthesized TiC; As the temperature up to 670°C continuously, $\text{Ti}_{(s)} + \text{C}_{(s)} = \text{TiC}_{(s)}$ takes place accompanying with $2\text{Fe}_{(s)} + \text{Ti}_{(s)} = \text{Fe}_2\text{Ti}_{(s)}$, and the conversion degrees of these reactions are increasing gradually. However, a part of Fe_2Ti will be decomposed with the temperature increasing further, and $\text{Ti}_{(s)} + \text{C}_{(s)} = \text{TiC}_{(s)}$ will go on because of the addition Ti. Consequently, the synthesized product consist of Fe, TiC and a little of Fe_2Ti , and ultrafine TiC particles distribute in the Fe matrix uniformly.

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