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Kinetics of thermite reaction in Al-Fe_2O_3 system

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Abstract

After non-isothermal differential scanning calorimetry (DSC) and X-ray diffraction experiments are carried out, the reaction kinetics of Al-Fe_2O_3 system is analyzed by a model-free Starink method. In our study, activation energy was determined as 145 kJ/mol for 8Al-3Fe_2O_3 thermite reaction, the value is comparable to the activation energy for diffusion of Al in $FeAl_2O_4$ and is less than the activation energy for diffusion of Al in Fe_3Al, suggesting that the diffusion of Al into $FeAl_2O_4$ controls the product of the thermite reaction.

Keywords: Differential scanning calorimetry; Thermite reaction; Kinetics

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1. Introduction

The Al-Fe_2O_3 system is well known by the exothermic reaction that it undergoes when submitted to thermal and/or mechanical treatments [1]. According to the following stoichiometric reaction:

$$8Al + 3Fe_2O_3 \rightarrow 2Fe_3Al + 3Al_2O_3, \qquad (1)$$

the final phases, Al_2O_3 and Fe_3Al intermetallics, are formed by an in situ chemical reaction in which Al reduces the iron oxide. Thermite reactions have become important in the synthesis of composites, in which the individual advantage of each constituent may be utilized to its best, achieving excellent mechanical properties of the composite as a whole. Moreover, thermite reaction is one of the methods commonly used to synthesize Fe-based magnetic particles dispersed in Al_2O_3. The magnetic particle systems, with single domain magnetic particles embedded in an insulating matrix, are interesting due to their applications in recording media, magnetic fluids for micro/nanoelectromechanical systems, catalytic reactions, or electromagnetic interference shielding and microwave absorbing applications, etc. [2].

However, due to the complexity of the reaction between liquid aluminum and Fe_2O_3, the preparation of composites with controlled phases and microstructure in a reproducible manner is still not satisfactory. The main difficulty is related to the complexity of the reaction with intermediate steps between the initial materials and the final product. Here, we investigate the reaction between Fe_2O_3 and Al by non-isothermal differential scanning calorimetry (DSC).

2. Experimental

Powder mixture of 8Al-3Fe_2O_3 (given in mol%) was prepared. The reagents used in this study consisted of commercial elemental powders of Al and Fe_2O_3. The powders were thoroughly mixed in a planetary mill for 30 min, and then cold-pressed to pellets of 10 mm in diameter under a uniaxial pressure of 100 MPa. The green compacts (weighing typically about 20–30 mg each) for thermal analysis were taken from the interior of the pellet.

Differential scanning calorimetry analyses at different heating rates from 5 to 20 K/min were carried out in a Netzsch DSC404 calorimeter. The DSC measurements were performed under a flow of high purity argon gas, utilizing high purity corundum as a reference.

The phases of the products after DSC experiment were identified by X-ray diffraction techniques. Rigaku D/max-rB(Japan)

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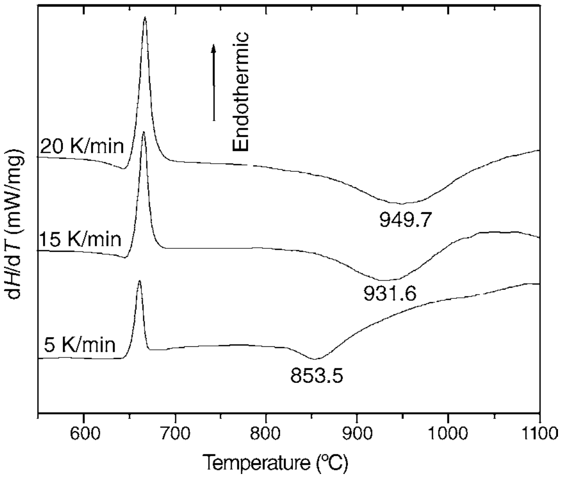

Fig. 1. DSC curves of 8Al-3Fe_2O_3 powder mixture at different heating rates.

diffractometer using Cu Kα radiation at 40 kV and 100 mA was employed to obtain chart recordings in the 2θ range from 35 to 80°.

3. Results and discussion

Fig. 1 shows the DSC curves of the 8Al-3Fe_2O_3 powder mixture at different heating rates. In each of the curves, the observed endothermic peak at about 660 °C is associated with the melting aluminum, while the exothermic peak represents the thermite reaction. Interestingly, the peak position is influenced significantly by the heating rates.

For the kinetics of thermally stimulated solid-state reactions, the following formula has been widely accepted:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha), \tag{2}$$

where α is the extent of reaction, t, the time, R, the universal gas constant, T, the temperature, $f(\alpha)$, the kinetic model function, and A and E_a are apparent pre-exponential factor and apparent activation energy, respectively.

In this paper, model-free approaches were used in kinetic evaluation. Model-free methods allow evaluation of the Arrhenius parameters without choosing the reaction model $f(\alpha)$. The best-known approaches, if several measurements with different heating rates and/or with different temperatures have been made, are the isoconversional methods according to Friedman [3] and the integral isoconversional method according to Kissinger [4] and Ozawa [5]. However, these methods are subject to approximations which can introduce significant inaccuracies in the determination of E_a. A new method for the derivation of activation energies is proposed by Starink [6]. It was shown [6] that this method is an order of magnitude more accurate than the Kissinger and Ozawa methods. These methods all comply with the following equation [6]:

$$\ln\left(\frac{T_P^s}{\phi}\right) = A\frac{E_a}{RT_P} + \text{constant}, \tag{3}$$

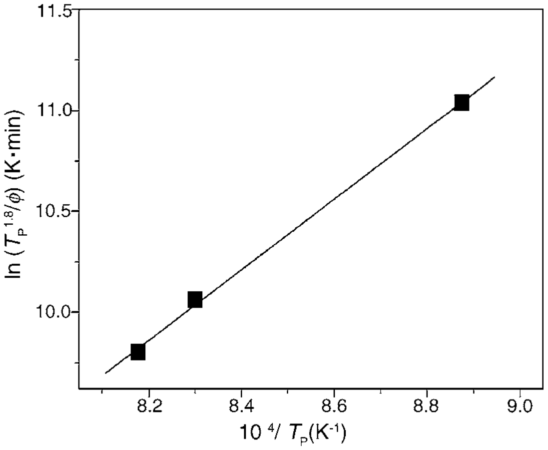

Fig. 2. Starink plot for the exothermic peak of the DSC curves, the determined activation energy is 145 kJ/mol.

where T_P is the peak temperature of the DSC curve, ϕ, the heating rate, s, a constant, and A is a constant which depends on the choice of s. In the case of Kissinger's method $s = 2$ and $A = 1$, the Ozawa methods $s = 0$ and $A = 1.0518$, while the Starink methods $s = 1.8$ and $A = 1.0070 - 1.2 \times 10^{-5}E_a$ (E_a in kJ/mol). We applied the latter method, and from the plot in Fig. 2 determined E_a of the 8Al-3Fe_2O_3 thermite reaction to be 145 kJ/mol.

For many oxides, studies of oxygen self-diffusion as well as metal ions diffusion show that Al and Fe are the more mobile species [7]. For the thermite reaction of 8Al-3Fe_2O_3 system, the most likely rate-controlling step is the diffusion of Al and/or Fe atoms. The XRD patterns of the products after DSC experiment is shown in Fig. 3, indicating that the presence of $FeAl_2O_4$, instead of thermodynamically predicted Fe_3Al intermetallic. Since the growth of product is governed by the diffusion of atoms, the value of activation energy (listed in Table 1) typical for the diffusion of Fe and/or Al in possible phase was used to characterize diffusion through the product. The value of the activation energy, 145 kJ/mol, for 8Al-3Fe_2O_3 thermite reaction in our study is comparable to the activation energy for diffusion of Al in $FeAl_2O_4$, and is less than the activation energy for diffusion of Al in Fe_3Al. It can be therefore be inferred that the diffusion of Al into $FeAl_2O_4$ controls the product of reaction.

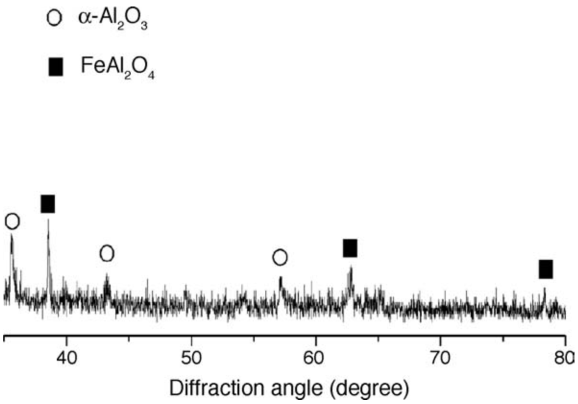

Fig. 3. XRD pattern of the products after DSC experiment at the heating rate of 20 K/min.

Table 1
The diffusion activation energy (kJ/mol) of Fe or Al in Fe_3Al, $FeAl_2O_4$ and Al_2O_3

Diffuser	Fe_3Al [8]	$FeAl_2O_4$ [9]	Al_2O_3 [7]
Fe	219	273	545
Al	223	162	477

4. Conclusion

According to thermodynamic prediction, the thermite reaction for 8Al-3Fe_2O_3 powder mixture results in alumina and Fe_3Al intermetallic when submitted to thermal treatments. Due to the kinetic effect, however, $FeAl_2O_4$ is formed in the solid-state reaction. Analysis of DSC data reveals that the activation energy for the thermite reaction is 145 kJ/mol, suggesting that the diffusion of Al into $FeAl_2O_4$ controls the product of reaction.

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