Study on Thermal Kinetics of nano Al/ micro MnO2 Thermite System

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Abstract. In order to explore the thermal kinetics of nano Al- micro MnO2 thermite system, the Al/MnO2 thermite sample was mixed by the ultrasonic dispersion method. On the basis of the study of thermal decomposition of MnO2 powder, the thermal performance of the sample was study by simultaneous thermal analysis technique at the temperature range from room temperature to 1000℃, which could found the thermite reaction occurred in 650-660℃ before the melting of Al, which belongs to solid state reactions with the 350 J/g heat releasing. Besides, the microstructure changes of the thermite during reaction were observed by field emission scanning electron microscope (FE-SEM). Based on the TG-DSC test with multiple heating rates and using of the activation energy calculated by Kissniger method, it could be proved the sample had good stability and safety performance.

1. Introduction

As a kind of energetic material with superior performance, aluminum heat agent has many advantages and characteristics which could be summarized as following aspects [1-4]: (1) Generally, the safety performance of aluminum thermo agent is superior and the threshold of various safety indexes such as friction, mechanical sensitivity, impact sensitivity and heat sense are high with good stability; (2) The temperature of the adiabatic flame can reach 2000~3000℃ [5] with high ignition temperature, rapid reaction and great reaction and discharge heat; (3) There are more selectable formulas, which can be mixed with a variety of common metal oxides and non-metal oxides according to the actual needs; (4) Under the reasonable ratio of each components, the complete self-supply of oxygen can be realized, ignoring the requirement for the reaction environment; (5) there are many sources of formula, and there is a certain substitution between each other, and the cost is low. [6]

On the other hand, the rapid development of material science cannot be separated from the continuous exploration and the discovery of new materials. At the same time, with the development and maturity of computer simulation and nano technology, it also provides new ideas and new directions for the improvement and research of traditional micron grade aluminum heat agents. S. G. Hosseini [7] selected CuO powders with two different particle sizes of 50nm and 180nm and mixed with micron grade Mg powder to prepare micro-nano composites. The reaction properties and thermal analysis kinetics were studied by differential calorimetric and equal conversion method, analyzing the effect of CuO with the same particle size on its reaction kinetics. In addition, due to the introduction of nanotechnology, the distance between metal oxide and fuel has been reduced effectively. According to Do Kyung Kim [8], the nano energetic materials were coated on the surface of CuO nanowires on the surface of the CuO nanowires under the pressure of 5*10^6 Pa, and the CuO/Al mixed powder was selected as the control group. The thermal performance and difference were compared by thermo-gravimetric differential thermal synchronous thermal analysis.
In view of the analysis of the above research status and the preliminary judgment of the future development of the aluminum heat agent, this paper mainly selected nano Al powder with micron grade MnO₂ and used ultrasonic blending to prepare the samples and studied its micromorphology and thermal properties [9]. According to the TG-DSC experimental results with multiple rates, the most classical Kissmiger method had been used for the samples. The activation energy was calculated, contributing to the knowing of the reaction characteristics and stability of samples.

2. Experiments

2.1. Materials
All chemicals were analytical reagent grade and were used without any further treatment or purification. Both 5μm-Al powder and 5μm-MnO₂ powder was purchased from Aladdin Industrial Corporation. (Shanghai, China).

2.2. Characterization and Thermal Analysis
In this paper, the nano-Al/micro-MnO₂ thermite was prepared through using ultrasonic mixing method. And the thermal properties and morphologies of the thermite were tested through the same TG-DSC (NETZSCH STA 449F3, Germany) analysis and field emission scanning electron microscope (FE-SEM) analysis (HITACHI High-Technologies Corporation, S-4800 II, Japan).

3. Results and Discussion

3.1 The results of FE-SEM
Firstly, scanning electron microscope (SEM) was used to observe the mixing of micron MnO₂/ nano Al aluminum heat agent after drying and milling. As shown in Figure 1, the sheet or lump was micron grade MnO₂, and the smaller spherical particles were nano Al powders. At the same time, the mixing uniformity was unexpected according to the electron microscope photos, which could be account for that the difference of particle size was large and both two kinds of particle size were mismatch. On the other hand, nano Al was much seriously agglomerate, attaching to the surface of micron MnO₂.

![Figure 1 The FE-SEM picture of sample](image)

3.2 The results of TG-DSC
In order to explore the thermal properties of micron MnO₂/ nano Al aluminum heat agent, the samples were tested by TG-DSC synchronous thermal analysis under three groups of different heating rates with 8℃/min, 10℃/min and 14℃/min respectively. Each samples were weighed 24.923mg, 22.480mg and 24.704mg respectively and placed in the corundum crucible. In dynamic nitrogen atmosphere with 30mL/min flow rate, the scanning temperature had been from room temperature to 1000 degrees. The TG-DSC curves were obtained in experiments, as shown in Figure 2.
In Figure 2, the shapes of the TG-DSC curves measured by the 3 groups were similar, indicating that the experimental reproducibility was better. It is needed to be illustrated that the red curve indicates the change of the thermo gravimetric (TG) curve as the temperature rises; the black curve indicates the variation of the differential scanning calorimetric (DSC) curve with the increase of temperature; the peak of the DSC curve indicates the heat release and the downward expression of the absorption.

From Figure 2, it can be seen that there is mainly an endothermic peak and two exothermic peaks in the synchronous thermal analysis test of micron MnO₂/nano Al thermo agents, and the detailed parameters of each peak are listed in Table 1, as shown in Table 1.

Table 1 Detailed parameters of DSC curves at different heating rates.

| Heating rate °C/min | No. | Starting temp/°C | Peak temp/°C | Ending temp/°C | Heat release/Jg⁻¹ |
|---------------------|-----|-----------------|--------------|----------------|------------------|
|                     | endothermic peak A | 538.6 | 556.2 | 571.3 | 362.5 |
| 8                   | endothermic peak B | 653.5 | 655.9 | 657.4 | -102.5 |
|                     | endothermic peak C | 765.0 | 803.9 | 849.7 | 149.8 |
| 10                  | endothermic peak A | 543.9 | 561.1 | 575.0 | 392.3 |
|                     | endothermic peak B | 648.0 | 655.2 | 660.0 | -79.3 |
|                     | endothermic peak C | 776.9 | 804.5 | 840.5 | 100.2 |
| 14                  | endothermic peak A | 541.7 | 560.0 | 575.1 | 355.2 |
|                     | endothermic peak B | 649.4 | 656.1 | 661.0 | -95.5 |
|                     | endothermic peak C | 751.4 | 799.5 | 843.8 | 240.5 |
According to the red TG curves of 3 groups in Figure 2, when the temperature rose from room temperature to 300°C, there were about 1% of the heat weight drop signals while the accompanying DSC curves were in the normal state, and no obvious endothermic or exothermic peaks found. The analysis was resulted from the anhydrous ethanol mixture in experiments, leading to some ethanol remained on the surface of the sample and evaporated with the increase of temperature.

There was an obvious exothermic peak A seen in the interval of about 540 to 570°C in the 3 groups of DSC curves, which was much higher than the previous group of micron MnO2/ micron Al heat agent. The discharge heat which was obviously increased with the far below initial temperature of the reaction was the micron MnO2/micron Al aluminum heat agent, whose TG curve had no obvious fluctuation. Therefore, it can be concluded that this exothermic peak was contributed by the thermal reaction between Al and MnO2 with the Al thermal reaction transferring oxygen from MnO2 to Al, generating Al2O3 without mass change. It can be seen from the diagram that the initial temperature of the thermal reaction of Al and MnO2 was near 540°C, the end temperature was near 575°C, the peak temperature was near 560°C and the heat of the thermite test was more than 350J/g.

As the test temperature continues to rise, the DSC curve appeared a endothermic peak B, the starting temperature of the endothermic peak B was near 650°C, the end temperature was near 660°C, the peak temperature was near 652°C and the TG curve had no obvious change. It is judged that the Al powder with excessive and incomplete reaction in the sample reacted with the blowing gas nitrogen and the formation of aluminum nitride.

In the same way, as the temperature continues to rise, a new exothermic peak of C was followed by the 3 groups of DSC curves. At the same time, with the obvious increase of the heat weight, the TG curve increased obviously. The chemical reaction between the overdose of the Al powder and the nitrogen gas of the blowing gas had a chemical reaction, leading to the heat was released without the mass increased.

Figure 3 is the products collected after the TG-DSC test on 3 groups of different heating rates. It is observed that the products after the reaction having obvious stratification with the red soil in the upper layer and green greyish in the lower layer. The reasons for the difference are mainly due to the addition of highly active nano Al powder, which leads to the early starting temperature of the reaction. The solid state reaction between the two components appears before the melting of the aluminum powder, which is usually not as uniform as the solid liquid phase. Besides, it is also affected by some extent that the particle size difference between the micron MnO2/ nano Al thermo agent components is larger and the mixing uniformity is higher.

3.3 Dynamic calculation
According to the above results, using Matlab linear regression programming, \( x = [0.001205764, 0.001198681, 0.001194244] \) indicates the reciprocal of the peak point temperature of heat release at 8°C.
/min, 10°C/min and 14°C/min heating rate. 1/Tp, Tp means Thermodynamic temperature; y= [-11.3618, -11.1505, -10.8214] means the corresponding calculated values of $\ln \left( \frac{\beta}{T_p^2} \right)$. Line fitting was done with x and y to get the fitting straight line, as shown in Figure 4.

$$\ln \left( \frac{\beta}{T_p^2} \right)$$

Fig. 4 fitting curves of micro MnO2/ nano thermite Al by Kissinger method. The linear expression is: $Y=45330x+43.264$, the fitting correlation coefficient is $R^2=0.9671$. The activation energy is calculated to be $E=376.9$, and the pre exponential factor is $\ln A=50.5s^{-1}$.

4. Conclusion
Through the experimental study on nano Al- micro MnO2 thermite system, it could found the thermite reaction occurred in 650-660°C before the melting of Al, which belongs to solid state reactions with the 350 J/g heat releasing. Based on the TG-DSC test with multiple heating rates and using of the activation energy calculated by Kissniger method\cite{10}, it could be proved the sample had good stability and safety performance.

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