Study on Thermal Chemical Reaction of Al/MnO₂ Thermite

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Abstract. To explore the reaction characteristics and mechanism of Al/MnO₂ thermite, selecting the high purity micron grade Al and MnO₂ powder, 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 900°C, and the reaction products were analyzed by X-ray diffraction (XRD). The microstructure changes of the thermite during reaction were observed by field emission scanning electron microscope (FE-SEM). The results showed that the MnO₂ has two processes of thermal decomposition during the temperature rising, and the reaction products were Mn₂O₃ and Mn₃O₄, and the onset temperature were 498.3 oC and 781.5 oC, the heat release were -197.1 J/g and -57.4 J/g, respectively. Al/MnO₂ thermite reaction contained a variety of chemical reactions, including two thermal decompositions and thermite reactions. The Al powder melted at 648.9°C. The thermite reaction was started at 547.8°C, and the peak temperature was at about 590.3°C. The measured heat release was 323.9 J/g. Thermite reaction process coincides with the first thermal decomposition of MnO₂. And the heat release of thermite reaction completely covered the endothermic decomposition.

1. Introduction
Thermite was first discovered by German chemist Goldschmidt in 1895. During thermite reaction a lot of heat can be released, and the reaction product is usually another kind of elementary substance and oxide. One of the most typical thermite reactions is the reaction between Al and Fe₂O₃ [1,2]. Therefore, all kinds of particle sizes, morphologies of Al/Fe₂O₃ thermite have attracted many attentions from the researchers and scholars [3-5]. Hu [4] chose template method to prepare nano-Fe₂O₃ with pollen structure and then composite with nano-Al, and the properties of Al/Fe₂O₃ thermite with pollen structure were investigated. Yi Jiankun [5] studied the application of Al/Fe₂O₃ thermite in ammunition destruction, which could quickly melt through the metal shell mainly by using the hot slag. And then the main charge can be ignited to achieve the purpose of ammunition destruction.

However, if MnO₂ is chosen as oxidation of thermite, the total heat quantity is higher than many common metal oxides theoretically. For example, the heat of Al/MnO₂ thermite is higher about 20% than that of Al/Fe₂O₃ thermite [6]. Currently there are several literatures reporting the primarily ammunition destruction application of micron level of Al/MnO₂ thermite. After ignition, Al/MnO₂ thermite has obvious flame jet but little slag. So the metal shell is mainly melted by the energy of flame to finish the ammunition destruction [7,8]. To the best of our knowledge, Al/MnO₂ thermite currently lacks the basic thermal performance and characteristics research. In 1998, Shrang [9] calculated the activation energy of the Al/MnO₂ thermite (molar ratio: 5:1) based on isothermal experiment. But the information about particle size and purity was not reported clearly, and the
optimal molar ratio between Al and MnO₂ should be 4:3 according to chemical reaction equations
4Al+3MnO₂ → 2Al₂O₃+3Mn.

Therefore, based on the above analysis, in this paper, high purity of micron grade Al powder and MnO₂ was chosen as raw materials to prepare the Al/MnO₂ thermite through the ultrasonic dispersion. First of all, the thermal decomposition properties of MnO₂ were investigated by using the simultaneous thermal analysis technology and X-ray diffraction (XRD). And then the thermal reaction properties of Al/MnO₂ thermite were explored through many different methods to get a further understanding of its thermite reaction.

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 thermal decomposition properties of MnO₂ were verified by TG-DSC (NETZSCH STA 449F3, Germany) analysis firstly. Then, the phase of its production was characterized by using the XRD analysis (Bruker, D8 Advance, Germany). Next, the Al/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). Finally, we tested the phase and morphologies of thermite reaction production.

3. Results and Discussion

3.1. Test results and analysis of MnO₂
For fully understanding the thermal performance of the Al/MnO₂ thermite, first of all, the thermal decomposition properties of MnO₂ were verified by TG-DSC analysis. The sample mass was about 33.564mg and the heating rates were 10°C min⁻¹ in corundum crucible, covering the temperature range from room temperature to 900°C in argon atmosphere, as shown in Fig.1 and Table.1.

![Fig.1 The TG-DSC curve of MnO₂ powder](image)

| No.      | Onset temperature /°C | Peak temperature /°C | End temperature /°C | Heat release /J/g |
|----------|------------------------|----------------------|---------------------|------------------|
| Endo-peak-A | 498.3                  | 573.2                | 612.1               | -197.1           |
| Endo-peak-B | 764.5                  | 834.5                | 843.6               | -57.4            |
In Fig.1, black solid line represents the DSC curve while the black dotted line is TG curve. TG curve is relatively smooth from room temperature to 480°C. And with no endothermic or exothermic signal in the DSC curve, this stage has no reaction.

When the temperature rises to the range from 480 °C~600 °C, TG curve suddenly appears a significant decline signal (about -8.4%). And the falling speed is relatively fast. In the meantime, DSC curve has an obvious endothermic peak (about -197.1J/g). So according to previous research[10], MnO₂ has been decomposed with relatively fast reaction speed, and the reaction product should be Mn₂O₃. And the reaction equation is $2\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$. According to this reaction equation, the theoretical weight loss is 9.20%, which is similar to the experimental measurement result.

As temperature continues to rise, TG curve moves smoothly. And there is no obvious mass change between 600 °C~730 °C. And with no endothermic or exothermic signal in the DSC curve, this stage also has no reaction. But when the temperature rises further to the range from 730 °C~850 °C, TG curve suddenly appears a significant decline signal (about -3.1%) again. In the meantime, DSC curve has an obvious endothermic peak (about -57.4J/g). So according to previous research[10], this stage means that the first reaction product Mn₂O₃ has further decomposed to Mn₃O₄. And the corresponding reaction equation is $6\text{Mn}_2\text{O}_3 \rightarrow 4\text{Mn}_3\text{O}_4 + \text{O}_2$. According to this reaction equation, the theoretical weight loss is 3.07%, which is similar to the experimental measurement result, too. Finally, when the temperature rise to 900°C, either TG curve or DSC curve has appeared no obvious change signal. Namely, there is no chemical reaction.

To confirm the phase of the thermal decomposition products of MnO₂, some of MnO₂ sample was calcinated at 700 °C and 900 °C for 3 hours, respectively. Fig.2 shows the XRD results of the MnO₂ samples at room temperature, after 700 °C calcination and 900 °C calcination. As shown in Fig.2, no distinct anomalous peak can be found in all of three spectrums, indicating that the really high purity of the obtained product.

### 3.2. Test results and analysis of Al/MnO₂ thermite

The Al/MnO₂ thermite sample mass was about 14.387mg and the heating rates were 10°C min⁻¹ in corundum crucible, covering the temperature range from room temperature to 900 °C in argon atmosphere, as shown in Fig.3 and Table.2.
To confirm the phase of the thermal decomposition products of MnO₂, some of MnO₂ sample was calcinated at 700 °C and 900 °C for 3 hours, respectively. Fig.2 shows the XRD results of the MnO₂ samples at room temperature, after 700 °C calcination and 900 °C calcination. As shown in Fig.2, no distinct anomalous peak can be found in all of three spectrums, indicating that the really high purity of the obtained product.

In Fig.3, black solid line represents the DSC curve while the black dotted line is TG curve. Before 480°C, there is no obvious mass change. When the temperature rises to the range from 480 °C~600°C, TG curve appears a significant decline signal (about -4.5%), which is relatively a bit fewer decline because of the addition of Al powder. Apparently, this mass decline is caused by the first thermal decomposition of MnO₂. However, there is a clear and sharp exothermic peak A (about 323.9 J/g) rather than the endothermic peak in DSC curve at this stage. Namely, the thermite reaction has happened here.

In Fig.1, the weight loss of the first thermal decomposition is about -8.4%. Considering the addition of 30% Al powder, theoretically the corresponding weight loss should be about -5.88% rather than that of -4.5%, which means that only part of MnO₂ has been decomposed. Namely, the rest of MnO₂ has reacted with Al powder called thermite reaction. According to the law of conservation of mass, O elements only transfer between MnO₂ and Al. So the part of thermite reaction will not appear the change of mass. Therefore, there are two main reactions between 480°C~630°C, respectively the first thermal decomposition of MnO₂ and thermite reaction between MnO₂ and Al.

The DSC curve appears an endothermic peak B (about -38.4 J/g) around 660°C. According to the physical properties of Al powder, the endothermic peak B is caused by the melting of Al powder.

With the increase of temperature, DSC curve has two signals between 760°C~900°C, respectively endothermic peak C and exothermic peak D. And the detailed parameters of peak C and D are listed in Table.2. Combined with Fig.1, it is easy to recognize that the thermal decomposition of the rest of Mn₃O₄ causes the endothermic peak C, which also releases O₂ lead to the decrease of mass and produces Mn₃O₄. And TG curve has a decrease of mass about -0.1%. Then, the appearance of exothermic peak D represents the thermite reaction between Mn₃O₄ and molten Al.

In order to further verify the reaction products, the black reaction products are analyzed by XRD analysis. As shown in Fig.4 and Fig.5, the main components of reaction products are Al₂O₃, Mn and Mn₃O₄. In the XRD pattern, the Al elemental diffraction peak cannot be found. Namely, all of Al powder became Al₂O₃, which has been reacted with the oxide of Mn[11,12].
As shown in Fig.6, the microstructures and morphologies of MnO₂ powder, the mixture of thermite and reaction product are observed through FE-SEM. Fig.8(a) is the SEM image of MnO₂ powder. From the image, the morphology of MnO₂ powder is mainly irregular angular flake or block. Fig.8(b) is the SEM image of thermite mixture. And is Al powder with about 5μm particle size. Because of in micron-level, the phenomenon of agglomeration is not obvious. And the distribution is relatively well-proportional. Apart from the Al spherical particle, the rest is MnO₂ powder with irregular flake or block. Fig.8(c) is the SEM image of the black reaction product. The eggshell structures marked by red circle are Al₂O₃ shells which originally cover on the surface of Al powder. With the increase of temperature, the molten Al burst from the package of Al₂O₃ shells to participate in the thermite reaction. In addition, the original irregular angular structure of MnO₂ powder disappears from the Fig.8(c). Instead, there are so many particles with smooth surface appearing marked by red panes.

4. Conclusions

Through the experiment and analysis above, the following conclusions can be drawn:

(1) Through the TG-DSC and XRD experiment of MnO₂, the results showed that there were two steps of thermal decomposition of MnO₂ in the process of temperature rising from room temperature to 900°C. The first thermal decomposition occurred near the range of 500 °C to 600 °C (MnO₂→Mn₂O₃) with oxygen release and heat absorption (about -197.1J/g). The second thermal decomposition occurred near the range of 750 °C to 850 °C (Mn₂O₃→Mn₃O₄) with oxygen release and heat absorption again (about -57.4J/g).

(2) Combining with the investigation of thermal decomposition properties and products of MnO₂, the first decomposition was covered totally by the thermite reaction with heat release (323.9J/g). The thermite reaction mainly occurred between Al and MnO₂. The final products of thermite reaction were mainly Al₂O₃, Mn and Mn₃O₄ according to the XRD analysis.

(3) The reaction process of Al/MnO₂ thermite was not a simple oxidation-reduction reaction between MnO₂ and Al. Instead there were a variety of chemical reactions at least including two thermal decomposition of MnO₂, thermite reaction between MnO₂ and Al.
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