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Study on Thermal Chemical Reaction of Al/MnO_2 Thermite

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Abstract. To explore the reaction characteristics and mechanism of Al/MnO_2 thermite, selecting the high purity micron grade Al and MnO_2 powder, the Al/MnO_2 thermite sample was mixed by the ultrasonic dispersion method. On the basis of the study of thermal decomposition of MnO_2 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 MnO_2 has two processes of thermal decomposition during the temperature rising, and the reaction products were Mn_2O_3 and Mn_3O_4, and the onset temperature were 498.3°C and 781.5°C, the heat release were -197.1J/g and -57.4 J/g, respectively. Al/MnO_2 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 MnO_2. 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 Fe_2O_3[1,2]. Therefore, all kinds of particle sizes, morphologies of Al/Fe_2O_3 thermite have attracted many attentions from the researchers and scholars[3-5]. Hu[4] chose template method to prepare nano-Fe_2O_3 with pollen structure and then composite with nano-Al, and the properties of Al/Fe_2O_3 thermite with pollen structure were investigated. Yi Jiankun[5]studied the application of Al/Fe_2O_3 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 MnO_2 is chosen as oxidation of thermite, the total heat quantity is higher than many common metal oxides theoretically. For example, the heat of Al/MnO_2 thermite is higher about 20% than that of Al/Fe_2O_3 thermite[6]. Currently there are several literatures reporting the primarily ammunition destruction application of micron level of Al/MnO_2 thermite. After ignition, Al/MnO_2 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/MnO_2 thermite currently lacks the basic thermal performance and characteristics research. In 1998, Shrangi[9] calculated the activation energy of the Al/MnO_2 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 MnO_2 should be 4:3 according to chemical reaction equations $4Al+3MnO_2 \rightarrow 2Al_2O_3+3Mn$.

Therefore, based on the above analysis, in this paper, high purity of micron grade Al powder and MnO_2 was chosen as raw materials to prepare the Al/MnO_2 thermite through the ultrasonic dispersion. First of all, the thermal decomposition properties of MnO_2 were investigated by using the simultaneous thermal analysis technology and X-ray diffraction (XRD). And then the thermal reaction properties of Al/MnO_2 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-MnO_2 powder was purchased from Aladdin Industrial Corporation. (Shanghai, China).

2.2. Characterization and Thermal Analysis

In this paper, the thermal decomposition properties of MnO_2 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/MnO_2 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 MnO_2

For fully understanding the thermal performance of the Al/MnO_2 thermite, first of all, the thermal decomposition properties of MnO_2 were verified by TG-DSC analysis. The sample mass was about 33.564mg and the heating rates were 10ºC min^{-1} in corundum crucible, covering the temperature range from room temperature to 900 ºC in argon atmosphere, as shown in Fig.1 and Table.1.

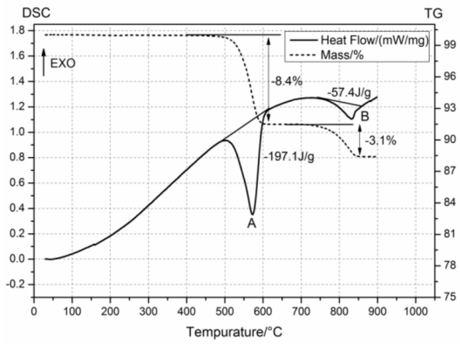


Fig.1 The TG-DSC curve of MnO_2 powder

Table 1 The parameters of endothermic peaks in the DSC curve

No.	Onset temperature /(ºC)	Peak temperature /(ºC)	End temperature /(ºC)	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 480ºC. 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 ºC~600 ºC, 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], MnO_2 has been decomposed with relatively fast reaction speed, and the reaction product should be Mn_2O_3. And the reaction equation is $4MnO_2 \rightarrow 2Mn_2O_3 + O_2\uparrow$. 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 ºC~730 ºC. 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 ºC~850 ºC, 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 Mn_2O_3 has further decomposed to Mn_3O_4. And the corresponding reaction equation is $6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2\uparrow$. 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 900ºC, 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 MnO_2, some of MnO_2 sample was calcinated at 700 ºC and 900 ºC for 3 hours, respectively. Fig.2 shows the XRD results of the MnO_2 samples at room temperature, after 700 ºC calcination and 900 ºC 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.

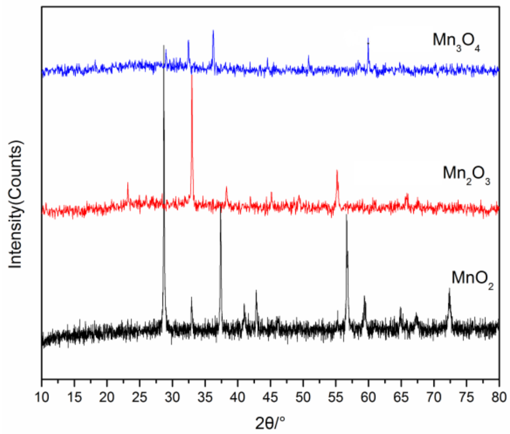


Fig.2 XRD spectrum of MnO_2 and its thermal decomposition products

3.2. Test results and analysis of Al/MnO₂ thermite

The Al/MnO_2 thermite sample mass was about 14.387mg and the heating rates were 10ºC min^{-1} in corundum crucible, covering the temperature range from room temperature to 900 ºC in argon atmosphere, as shown in Fig.3 and Table.2.

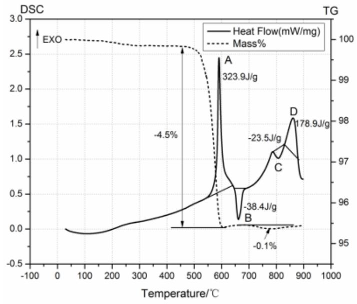


Fig.3 The TG-DSC curve of Al/MnO_2 thermite

Table.2 The parameters of endothermic and exothermic peaks in the DSC curve

No.	Onset temperature /(°C)	Peak temperature /(°C)	End temperature /(°C)	Heat release /(J/g)
Exo-peak-A	547.8	590.3	621.2	323.9
Endo-peak-B	649.8	661.6	677.1	-38.4
Endo-peak-C	776.5	812.3	826.1	-23.5
Exo-peak-D	821.3	861.1	883.7	178.9

To confirm the phase of the thermal decomposition products of MnO_2, some of MnO_2 sample was calcinated at 700 °C and 900 °C for 3 hours, respectively. Fig.2 shows the XRD results of the MnO_2 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.

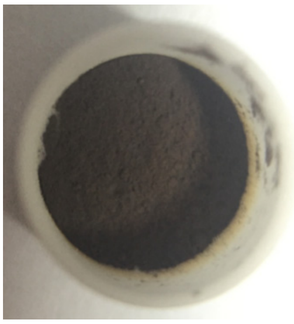
In Fig.3, black solid line represents the DSC curve while the black dotted line is TG curve. Before 480°C, there is no obvious mass change. When the temperature rises to the range from 480°C~600°C, TG curve appears a significant decline signal (about -4.5%), which is relatively a bit fewer decline because of the addition of Al powder. Apparently, this mass decline is caused by the first thermal decomposition of MnO_2. However, there is a clear and sharp exothermic peak A (about 323.9J/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 MnO_2 has been decomposed. Namely, the rest of MnO_2 has reacted with Al powder called thermite reaction. According to the law of conservation of mass, O elements only transfer between MnO_2 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 MnO_2 and thermite reaction between MnO_2 and Al.

The DSC curve appears an endothermic peak B (about -38.4J/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 easily to recognize that the thermal decomposition of the rest of Mn_2O_3 causes the endothermic peak C, which also releases O_2 lead to the decrease of mass and produces Mn_3O_4. And TG curve has a decrease of mass about -0.1%. Then, the appearance of exothermic peak D represents the thermite reaction between Mn_3O_4 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 Al_2O_3、Mn and Mn_3O_4. In the XRD pattern, the Al elemental diffraction peak cannot be found. Namely, all of Al powder became Al_2O_3, which has been reacted with the oxide of Mn[11,12].



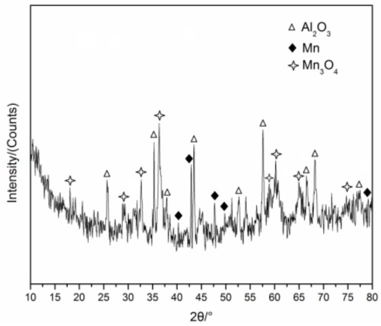
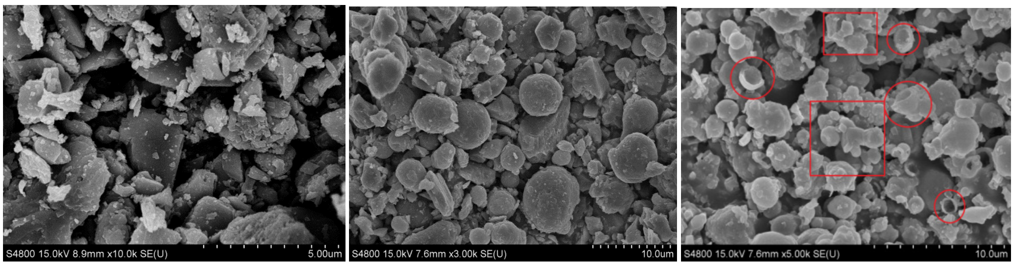


Fig.4 products after reaction Fig.5 XRD pattern of the reaction products

As shown in Fig.6, the microstructures and morphologies of MnO_2 powder, the mixture of thermite and reaction product are observed through FE-SEM. Fig.8(a) is the SEM image of MnO_2 powder. From the image, the morphology of MnO_2 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 MnO_2 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 Al_2O_3 shells which originally cover on the surface of Al powder. With the increase of temperature, the molten Al burst from the package of Al_2O_3 shells to participate in the thermite reaction. In addition, the original irregular angular structure of MnO_2 powder disappears from the Fig.8(c). Instead, there are so many particles with smooth surface appearing marked by red panes.



(a) powder of MnO_2 (b)before the reaction (c) after the reaction

Fig.6 FE-SEM image of the Al/MnO_2 thermite before and after reaction

4. Conclusions

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

(1) Through the TG-DSC and XRD experiment of MnO_2, the results showed that there were two steps of thermal decomposition of MnO_2 in the process of temperature rising from room temperature to 900ºC. The first thermal decomposition occurred near the range of 500 ºC to 600 ºC ($MnO_2 \rightarrow Mn_2O_3$) with oxygen release and heat absorption (about -197.1J/g). The second thermal decomposition occurred near the range of 750 ºC to 850 ºC ($Mn_2O_3 \rightarrow Mn_3O_4$) with oxygen release and heat absorption again (about -57.4J/g).

(2) Combining with the investigation of thermal decomposition properties and products of MnO_2, the first decomposition was covered totally by the thermite reaction with heat release (323.9J/g). The thermite reaction mainly occurred between Al and MnO_2. The final products of thermite reaction were mainly Al_2O_3, Mn and Mn_3O_4 according to the XRD analysis.

(3) The reaction process of Al/MnO_2 thermite was not a simple oxidation-reduction reaction between MnO_2 and Al. Instead there were a variety of chemical reactions at least including two thermal decomposition of MnO_2, thermite reaction between MnO_2 and Al.

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