THERMAL REACTION PROCESSES AND CHARACTERISTICS OF AN Al/MnO₂ PYROTECHNIC CUTTING AGENT BASED ON RESIDUE ANALYSES

TERMIČNO REAKCIJSKI PROCESI IN LASTNOSTI PIROTEHNIČNEGA REZALNEGA SREDSTVA Al/MnO₂ NA OSNOVI ANALIZE OSTANKOV

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The pyrotechnic cutting performance of an Al/MnO₂ mixture was carried out via an onset experiment. In order to understand the thermal reaction processes of the sample, both the oxide component (MnO₂) and the mixture were tested by simultaneous thermal analysis. The chemical reaction processes were analysed based on residue analysis. There was an obvious combustion flame during the thermal reaction of the Al/MnO₂ pyrotechnic cutting agent, and the flame could melt through the steel target easily, which meant Al/MnO₂ thermite mixture had a good pyrotechnic cutting performance. Thermal reactions between Al and MnO₂ had several chemical processes, including two thermal decompositions process of MnO₂ and thermite exothermic reactions. As for the main exothermic reaction, the measured heat release was about 323.9J g⁻¹ in the temperature range from 547.8 °C to 641.6 °C before the Al melt. The reaction products were mainly MnO (manganosite) and Al₂O₃.

Keywords: simultaneous thermal analysis, pyrotechnic cutting agent, manganese dioxide

Avtorji v članku na osnovi izvedenih preizkusov poročajo o pirotehničnih lastnostih mešanice prahov Al in MnO₂. Da bi razumeli termično reakcijske procese vzorca, so izvedli simultano termično analizo tako oksidne komponente (MnO₂), kot tudi mešanice. Kemijske reakcijske procese so analizirali s pomočjo analize ostankov. Nastal je očiten plamen med termično reakcijo pirotehničnega rezalnega sredstva Al/MnO₂ in posledično je plamen zelo lahko enostavno raztalil oz. preluknjal jekleni vzorec (ploščo), kar pomeni da ima izbrana termitna mešanica Al/MnO₂ dobre pirotehnične sposobnosti za rezanje. Reakcija med Al in MnO₂ je potekala v dveh fazah: s termičnim razpadom MnO₂ in z eksotermičnimi reakcijami. Glavna eksotermična reakcija je potekala med 547,8 °C in 641,6 °C še preden je prišlo do taljenja Al. Pri tem procesu so avtorji izmerili sproščanje toplote na približno 323,9 J·g⁻¹. Reakcijska produkta sta bila v glavnem MnO (manganozit) in Al₂O₃.

Ključne besede: simultana termična analiza, pirotehnično rezalno sredstvo, manganov dioksid

1 INTRODUCTION

Thermite, as a kind of energetic material, is composed of two components: fuel and oxidizer, which could be used as the pyrotechnic cutting agent.[1,2] Usually, magnesium (Mg) and aluminium (Al) powder can be chosen as the fuel. For instance, as for Mg/CuO thermite mixture, Hosseini reported that the particle size of the metal oxide would significantly affect the thermal behaviour of the thermite system.[3] In fact, compared with Mg powder, the volumetric combustion heat of Al powder is much higher than that of Mg powder.[4] Besides, Al has the advantages of high energy density, lower cost, many more resources and a lower melting temperature than that of Mg powder, theoretically. So, Al-based thermite is one of the most widely used energetic materials for many applications, such as explosives, electric igniters, welding and propellants.[5–8]

As for the oxidizer, there are so many metallic or non-metallic oxides to be used in a thermite system, such as Fe₂O₃, NiO, I₂O₅, Bi₂O₃ and CuO. Hu synthesized pollen-like porous Fe₂O₃ via a template method, then the Fe₂O₃ was combined with Al powder to prepare the Al/Fe₂O₃ thermite energetic composite.[9] According to Hu's results, pollen-like Al/Fe₂O₃ thermite mixture has good compatibility with both Hexogen (RDX) and Octogen (HMX), but it is not compatible with Hexa-droitrohexazoiso-woods Alkyl (CL-20) and Glycidyl Azide Polymer (GAP) based on the results of TG-DSC tests. Al/NiO nanothermite film has been synthesized and prepared via integrating a colloidal crystal template and magnetron sputtering, and it shows a uniform structure and homogeneous density with greatly improved interfacial contact between the fuel and the oxidizer on the nanoscale.[10] A. M. Hobosyan[2] chose I₂O₅ as an oxidizer to prepare nanostructure energetic materials. The experiments showed that the nanostructured Al/I₂O₅ energetic materials have a pressure

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discharge value of 43.4M Pa/g, which is twice that of the purchased commercial micro-level I_2O_5 particles. L. Glavier11 and his co-authors reported four kinds of thermite powder mixtures and their burning rate performances and over-pressure generation, Al/Bi_2O_3, Al/MoO_3, Al/CuO and $Al/PTFE$.[11] They observed that the Al/Bi_2O_3 powder mixture has the fastest burning rate, while $Al/PTFE$ has the slowest velocity, and Al/CuO thermite mixture could generate the highest pressure peak. CuO, as an oxidizer, is one of the most widely used in the thermite system. Unlike other oxidizers, CuO has a thermal decomposition process with gaseous oxygen release when heated. This unique property has a great influence on the reaction mechanism of the Al/CuO thermite system. Sui prepared an Al/CuO nanothermite composite with a layer-by-layer structure, and they found that the thermite reaction between Al and CuO nanoparticles was initiated, at the onset temperature, by the interactions of Al and CuO nanoparticles at the contacting surface of the two reactive layers.[12] Then, the thermal-decomposition of CuO occurs, followed by the subsequent migration of oxygen into the Al layer. The thermite reaction was maintained by the gas-solid reaction between the Al nanoparticles and oxygen.

As for the thermal decomposition properties of oxidizers, the characteristics of MnO_2 are similar to CuO. The process and kinetics of the thermal decomposition of MnO_2 have been reported. The results showed that there are two main reactions during the thermal decomposition, $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4$.[13,14] According to Fisher's famous report, the theoretical calculation reaction heat of $4Al+3MnO_2$ is higher than that of the Al+CuO system.[15] Recently, the thermal properties and kinetics of $Al/\alpha\text{-}MnO_2$ nanostructure thermite have been reported, and its heat release was approximately 1150J g^{-1}.[16] Al/MnO_2 nanothermite, as a kind of additive, has been added into propellants as well as explosives.[17,18] Besides, a pyrotechnic cutting agent is an important use for thermites.

As for pyrotechnic cutting agent, a large dosage of Al/MnO_2 nanothermite, for example more than ten grams of sample, will lead to a sudden explosion because of the high energy density and the fast reaction speed, and the prices of nanomaterials are usually much higher than those of micron-level materials. In addition, the preparation process of micron-level thermite is simple and effective. Therefore, technical staff and industries prefer to use micron-level components rather than nano-level thermites in engineering applications, at present. In this paper we report and analyse the pyrotechnic cutting performance of Al/MnO_2 pyrotechnic cutting agent mixture at the micron-level scale, and the morphologies and phase characteristics of the sample are tested by field emission scanning electron microscope (FE-SEM), X-ray diffraction(XRD) and simultaneous thermal analysis. In the end, the reaction products are collected

and tested. Based on residue analysis, the possible chemical reaction is analysed.

2 EXPERIMENTAL PART

2.1 Materials and equipments

Al powder, Shanghai Naiou Nano Technology co., LTD., purity >99.9 %, average particle size 5 μm; MnO_2 powder, Shanghai Naiou Nano Technology co., LTD., purity >99.9 %, average particle size 5 μm; Anhydrous ethanol, AP, Shanghai Jiuyi Chemical Reagent co., LTD. All the reagents were used directly without any further treatment or purification.

The Al/MnO_2 pyrotechnic cutting agent mixture phase and chemical components were characterized using XRD analysis (Bruker, D8 Advance, Germany). The morphologies, particle size and mixing quality of the components and Al/MnO_2 pyrotechnic cutting agent mixture were characterized by FE-SEM analysis (HITACHI High-Technologies corporation, S-4800 II, Japan). The investigation of thermal behaviour was carried out based on the TG-DSC (NETZSCH STA 449F3, Germany) analysis, and the heating rate was 10 °C min⁻¹ in a corundum crucible, covering the temperature range from room temperature to 900 °C in a N_2 atmosphere with a velocity of 30 mL min⁻¹.

2.2 Sample preparation

The Al/MnO_2 pyrotechnic cutting agent mixture was prepared through the use of the ultrasonic mixing method. Prior to the mixing process, 30.0 g of Al powder and 70.0 g of MnO_2 powder (mass fraction ratio of Al/MnO_2 about 3:7) were immersed in anhydrous ethanol with magnetic stirring separately for 30 min. Then, both mixed liquids were sonicated for 30 min, primarily in a sonic bath (Hechuang, KH3200E). Next, the ethanol solution of Al was slowly and homogeneously added into the ethanol solution of MnO_2. The suspension was ultrasonically dispersed and magnetically agitated for several times until the ethanol was almost evaporated to dryness under ambient conditions. After the ultrasonic mixing operation, the slurry was dried at 60 °C for 12 h under vacuum. The thermite mixture was poured into a firework torch. The torch was prepared from PVC pipe scrap.

2.3 Pyrotechnic cutting experiment

Figures 1a and **1b** are the diagram and photograph of the pyrotechnic cutting onset experiment, respectively. The ignition device was installed on the top of Al/MnO_2 pyrotechnic cutting agent and was sparked by electric firing. Before ignition, the 3-mm steel plate was set on the upper part of pyrotechnic cutting agent. The distance between the surface of the pyrotechnic cutting agent and the steel plate was about 3 cm. The process of ignition and combustion was recorded by a camera.
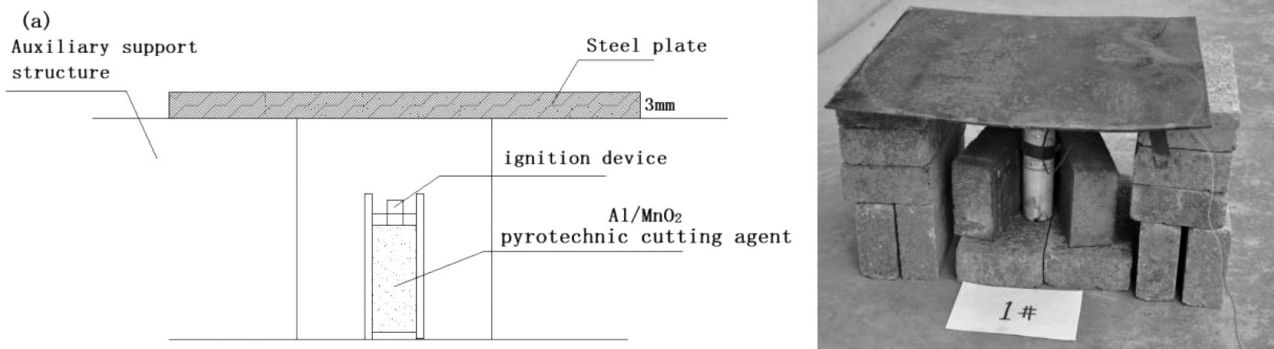
Figure 1: Pyrotechnic cutting onset experiment of: a) setting diagram, b) experiment photo

3 RESULTS AND DISCUSSION

3.1 Pyrotechnic cutting performance

Figure 2 shows the process of the Al/MnO₂ pyrotechnic cutting agent combustion experiment to test its pyrotechnic cutting performance. The Al/MnO₂ pyrotechnic cutting agent was ignited electrically. As shown in **Figure 2a**, the colour of the fire is white at the beginning of the pyrotechnic cutting agent combustion. Then so much thermite mixture is ignited because of the self-propagation reaction, and the fire becomes saffron yellow in a very short time, **Figure 2b**. The flame heats directly on the lower surface of the steel plate. Next, the steel plate is melted through suddenly, and according to **Figure 2c**, the height of the flame is about 100 cm, so there must be a certain pressure on the steel plate before melting through. In **Figure 2d**, the height of the flame still high, about 100 cm, which means that the combustion of the Al/MnO₂ pyrotechnic cutting agent could last for some time, about several seconds. In the end, the height of flame gradually becomes low in **Figure 2e**. Besides, as shown in **Figures 2c** to **2e**, there is a lot of

smoke during the combustion. The whole process lasts about 35 s.

Figure 3 presents the results of the Al/MnO₂ pyrotechnic cutting agent combustion experiment, which could verify its pyrotechnic cutting performance. As shown in **Figures 3a** and **3b**, there is apparently a burnt hole in the steel plate, and there is a deposit of molten steel around the hole. In order to quantify the pyrotechnic cutting performance, we measured the hole in **Figures 3c** and **3d**. The hole is shaped like a short strip. The width is about 1.0 cm and the length is about 3.5 cm.

In order to understand the phenomenon of the combustion experiment, we made further research on the component and pyrotechnic cutting agent.

3.2 TG-DSC results

Figure 4 presents the results of the TG-DSC tests. The black line is the DSC curve in the range of room temperature to 900 °C while the blue line is the TG curve.

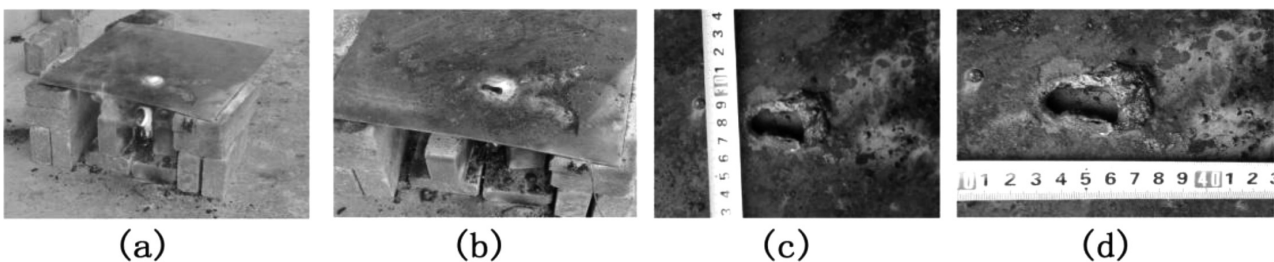**Figure 2:** The Al/MnO₂ pyrotechnic cutting agent combustion experiment

Figure 3: The result of the Al/MnO₂ pyrotechnic cutting agent combustion experiment

Before the temperature reached 500 °C, there is no obvious signal in either the DSC curves or TG curves, which means that there is no chemical reaction. Figure 4a is the TG-DSC results of the MnO_2 component. In the temperature range 500 °C to 600 °C, a rapid mass loss appears in the TG curve, about –8.5 %, and the endothermic peak A appears in the DSC curve with heat release –197.1J g⁻¹, which means the first thermal decomposition of MnO_2. As the temperature continues to rise, there is no endothermic or exothermic signal with the smooth TG curve. But when the temperature rises to 730 °C, the second mass loss signal appears in the TG curve, about –0.9 %, the heat release is about –57.4 % (Endothermic Peak B).

Figure 4b is TG-DSC results of the Al/MnO_2 pyrotechnic cutting agent. In the temperature range of 500 °C to 600 °C, due to the thermal decomposition performance of the MnO_2 component, there is also a rapid mass loss in the TG curve, about –4.3 %, and there is no endothermic signal but an apparent exothermic peak (Exothermic Peak C) with 323.9J g⁻¹ heat release. As is generally known, Al powder will not decompose in this temperature range. As the mass fraction of Al powder added is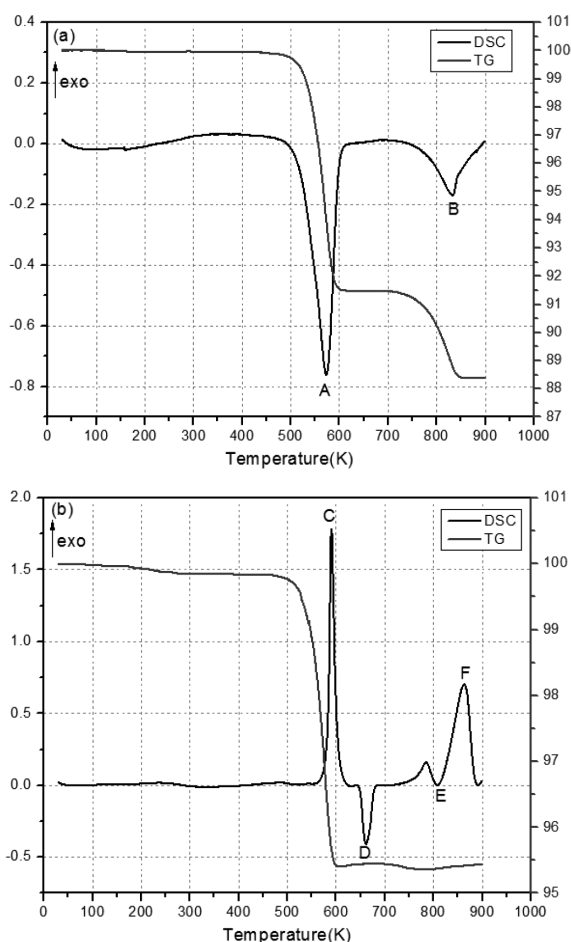 about 30 %, the theoretical mass loss should be reduced by about –5.9 % if all of MnO_2 in pyrotechnic cutting agent is decomposed. But in fact, the experimental measurement value of the mass loss is only –4.3 %. It means that only part of the MnO_2 component undergoes the first thermal decomposition and the rest directly reacts with Al powder in the solid state. According to the law of conservation of mass, the oxygen element only transfers between MnO_2 and Al powder, so the part of thermite reaction will not show a mass change.

As for the thermal decomposition product, according to the position of the peak point of exothermic peak C, the most intense reaction point (peak C) appears after the mass reduction is completed in the TG curve, which means the thermal decomposition product involves in the thermal chemical reaction. Therefore, between 500 °C and 600 °C, there are at least three intertwined reactions. They are the first thermal decomposition reaction of MnO_2, the thermite reaction of MnO_2 with Al and the reaction between decomposition products of MnO_2 with Al.

Peak C is the main reaction with a lot of gaseous oxygen release, which could be the main reason why in **Figure 2c** and **2d** the height of thermite flame is so high. Gaseous oxygen has a good combustion-supporting effect. It could greatly increase the combustion temperature of the flame, which is one of the reasons why the steel plate is melted. Besides, the participation of gaseous oxzgen will increase the speed of combustion and increase the combustion pressure. The high temperature causes the surface of the steel sheet to melt, while the high combustion pressure causes the steel sheet to be perforated.

Around 660 °C, the endothermic peak (D) appears on the DSC curve. According to the properties of Al powder, the endothermic peak (D) is caused by the melting heat absorption of Al powder, about –38.4J g⁻¹.

With the increase of temperature, between 760 °C and 900 °C, the DSC curve has two signals, and endothermic peak E and exothermic peak F, respectively. The main reason for the appearance of the endothermic peak E is the further thermal decomposition, which does not undergo the thermite reaction. The further thermal decomposition will also be released gaseous oxygen with a mass reduction, about –0.2 %. The exothermic peak F appears after the endothermic peak E, which might be the second thermite reaction between the further thermal decomposition products and the melted Al powder. There is no obvious mass change in the second thermite reaction according to the law of mass conservation.

3.3 XRD results

In order to figure out the phase of the thermal decomposition products, an adequate amount of MnO_2 sample is calcinated in a muffle furnace, and the calcination temperature is 700 °C and 900 °C, respectively, with 3 hof thermal insulation, respectively, with the product
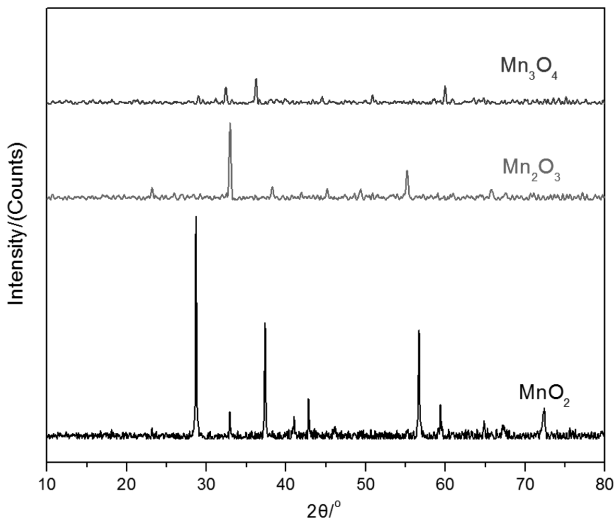

Figure 4: Results of TG-DSC tests: a) MnO_2 component, b) Al/MnO_2 pyrotechnic cutting agent

peak and the characteristic peak of the product (the red spectrum) are consistent with Mn$_2$O$_3$ (JCPDS PDF 41-1442), and after 900 °C calcinations, the XRD diffraction peak and the characteristic peak of the product (the blue spectrum) are consistent with Mn$_3$O$_4$ (JCPDS PDF 24-0734).

After the TG-DSC experiment, the residues of Al/MnO$_2$ pyrotechnic cutting agent sample were collected, which should be the reaction products. The residues of the Al/MnO$_2$ sample in crucible, mainly grey-green solid substances, are shown in **Figure 6**. The reaction products of the Al/MnO$_2$ pyrotechnic cutting agent are tested by XRD, as shown in **Figure 6**. The main components of the products are Al$_2$O$_3$ and MnO, instead of Mn or Mn$_3$O$_4$. MnO, as a common manganese oxide, is grey-green. According to a previous research report, the oxides in the metal elemental manganese are only MnO and Mn$_3$O$_4$, and the amount of MnO will continue to increase if the temperature is above 800 °C.[19] In our experiment the sample is heated up to 900 °C. In addition, due to the thermite reaction occurrence, the products are mainly MnO, which is consistent with the grey-green colour and the XRD spectrum. So, the chemical reaction equation of the Al/MnO$_2$ pyrotechnic cutting agent should be as follows:

$$2Al + 3MnO_2 \rightarrow MnO + Al_2O_3 \tag{1}$$
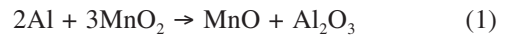
3.4 SEM results

As shown in **Figure 7**, the morphology of MnO$_2$ powder and the microstructure of the Al/MnO$_2$ pyrotechnic cutting agent before and after the thermal reaction are observed by FE-SEM. **Figure 7a** is a FE-SEM image of MnO$_2$ powder, and the microstructure of the MnO$_2$ is an irregular sheet or block with distinct edges and corners. **Figure 7b** is a FE-SEM image of the Al/MnO$_2$ pyrotechnic cutting agent before the thermal reaction. The spherical particles are Al powder with a 5-μm particle size, and there is no obvious agglomeration. The distribution is more dispersed, and the irregular sheet or block sample is MnO$_2$. From the picture, there is no reaction at normal temperature, which means the two components can coexist.

Figure 7c is a FE-SEM image of the product after the thermal reaction. The eggshell structure in the red circle in the **Figure 7c** is the Al$_2$O$_3$ layer formed by the oxidation of the surface of Al powder. As the temperature increases, the molten Al breaks out from the wrapped Al$_2$O$_3$ film and participates in the reaction, leaving the Al$_2$O$_3$ shell. The increase in the thickness of the shell is due to the partial adhesion of Al to the initial Al$_2$O$_3$ layer during the rupture process, resulting in an increase in thickness. In addition, it can be seen from the **Figure 7c** that the irregular angular or block structure of the original MnO$_2$ disappears and is replaced by the smoother particles on the inner surface of the red square in the **Figure 7c**. The reaction products are agglomerated due

Figure 5: XRD spectrum of MnO$_2$ and its thermal decomposition products

removed after cooling. The XRD spectrum of MnO$_2$ and its thermal decomposition products are shown in **Figure 5**. After 700 °C calcinations, the XRD diffraction
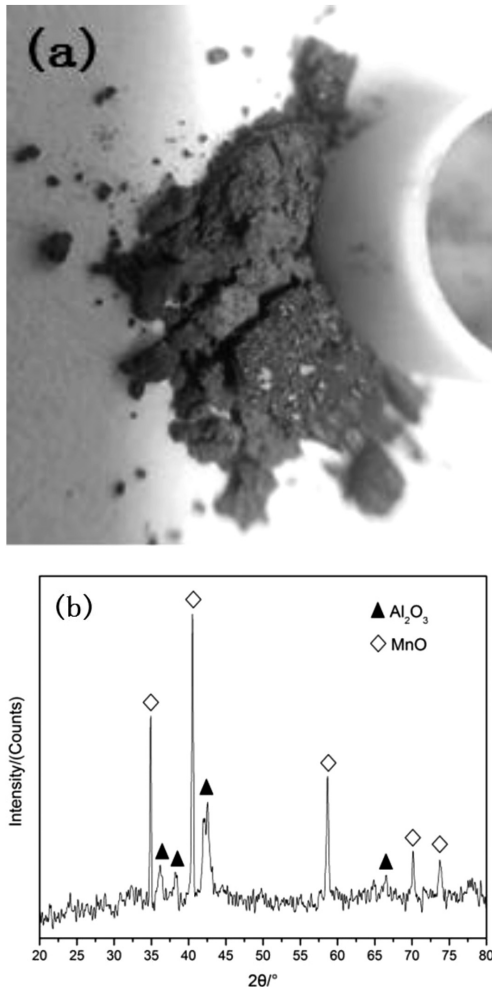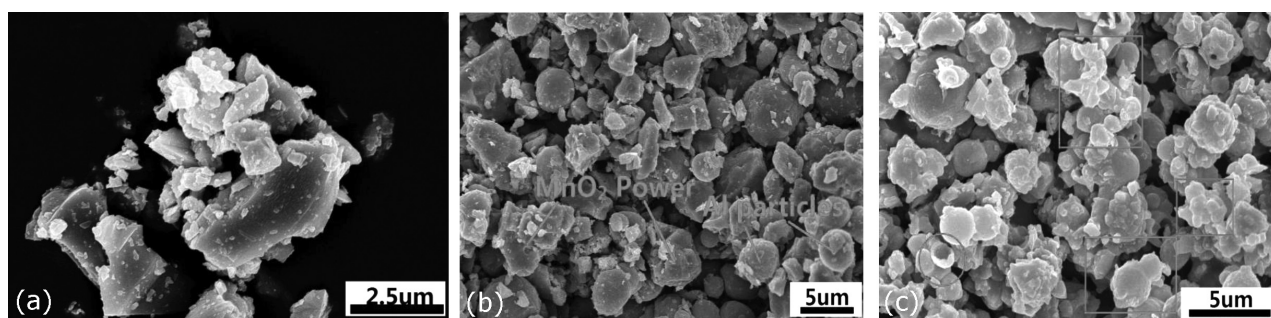

Figure 6: Results of reaction products: a) residues in crucible, b) the XRD spectrum

Figure 7: FE-SEM images of samples: a) MnO$_2$ powder, b) Al/MnO$_2$ agent mixture before thermal reaction, c) Al/MnO$_2$ agent mixture after thermal reaction

to the high temperature and the chemical reaction. The small sphere in **Figure 7c** is the Al$_2$O$_3$ product after the Al powder reaction, and the volume is significantly smaller than the Al-Al$_2$O$_3$ ball before the reaction.

4 CONCLUSIONS

In paper, the pyrotechnic cutting performance of Al/MnO$_2$ thermite is reported. It can burn a 3-mm steel plate with a hole that is 3.5 cm long and 1 cm wide in 35 s. Firstly, the thermal decomposition performance of MnO$_2$ was verified by TG-DSC and XRD. In order to explain the combustion phenomenon, an Al/MnO$_2$ thermite sample was tested by TG-DSC. A large amount of MnO$_2$ in the Al/MnO$_2$ thermite system decomposes and releases gaseous oxygen, while the rest of MnO$_2$ reacts with the Al powder, a solid phase reaction. At the same time, according to the position of the peak (A), thermal decomposition product Mn$_2$O$_3$ is also involved in a thermite reaction. Gaseous oxygen has a good combustion-supporting effect. It could greatly increase the combustion temperature of the flame, which is one of the reasons why the steel plate is melted. Besides, the participation of gaseous oxygen will increase the speed of combustion and increase the combustion pressure. The high temperature causes the surface of the steel sheet to melt, while the high combustion pressure causes the steel sheet to be perforated. According to the image and the XRD spectrum of the reaction products in the crucible, a lot of grey-green solid substances should be MnO rather than Mn. It means that the chemical reaction equation of the Al/MnO$_2$ thermite system is 2Al+3MnO$_2$ → 3MnO+Al$_2$O$_3$. Finally, the morphology of the MnO$_2$ powder and the microstructure of the Al/MnO$_2$ thermite before and after the reaction are observed by FE-SEM. The microstructure of MnO$_2$ is an irregular sheet or block, with distinct edges and corners. As the temperature increases, the molten Al breaks out from the wrapped Al$_2$O$_3$ film and participates in the reaction, leaving the Al$_2$O$_3$ shell.

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