Effect of MnO₂ morphology on the thermal properties and combustion behavior of nano-Al/MnO₂ thermite

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Abstract

Al/granular MnO₂ and Al/rod MnO₂ thermite samples were prepared to investigate the effects of different morphologies of MnO₂ on the thermal properties and combustion behavior of nano-Al/MnO₂ thermite. The morphology and thermal properties of the thermite were characterized by field emission scanning electron microscopy (FE-SEM), x-ray diffractometry (XRD), and differential scanning calorimetry (DSC). DSC results show that the Al/rod MnO₂ releases 1274.39 J·mol⁻¹ heat, which is 292.58 J·mol⁻¹ more than the Al/granular MnO₂. The initial reaction temperature of Al/rod MnO₂ is 567.39 °C, which is delayed by 17.39 °C versus 550 °C of Al/granular MnO₂. Non-isothermal thermodynamic analysis was used to measure the activation energy of Al/rod MnO₂ to be 234.36 kJ·mol⁻¹, which is 46.53 kJ·mol⁻¹ higher than that of Al/granular MnO₂. This corresponds to an increase in the ignition temperature in the DSC curve and indicating a higher safety profile. In the open burning experiment, the burning time of Al/granular MnO₂ was longer and sparks sputtered around the flame. The Al/rod MnO₂ has a large combustion flame and a fast combustion rate. The light intensity peaks of the two groups of samples are close in the light intensity test. The light intensity existence time of Al/rod MnO₂ is 0.0146 s, which is 0.094 s shorter than Al/granular MnO₂. This shows that the combustion rate of Al/rod MnO₂ is much faster than that of Al/granular MnO₂. The closed-tube combustion experiment shows that the combustion wave velocity of Al/rod MnO₂ increases first and then decreases; the maximum wave velocity reaches 339.6 m·s⁻¹, and Al/granular MnO₂ cannot self-propagate combustion in the microporous environment. In the constant volume combustion experiment, the peak combustion pressure of Al/rod MnO₂ is 0.938 Mpa, and the peak value of Al/granular MnO₂ combustion pressure is 0.581 Mpa; the difference is obvious. This shows that the rod MnO₂ gas production performance is better. According to the duration of the pressure peak, the burning speed of Al/rod MnO₂ in the light intensity test is confirmed again to be much faster than that of Al/granular MnO₂. The Al/rod MnO₂ is better than Al/granular MnO₂ in thermal and combustion performance and is also safer. This provides a basis for future performance and safety research on aluminothermic materials.

1. Introduction

Thermite has attracted the attention of many researchers because of its high combustion efficiency, high energy release rate, and good reaction release enthalpy. Thermite is widely used in welding and gas generation [1–3], and it is a high-energy additive. Recently, nano thermite has attracted much attention owing to its large specific surface area and smaller particle spacing [4].

Thermites generally consist of metal oxides and metal powders. In the selection of metal powders, aluminum offers a high exotherm per unit density, good reactivity, and non-toxic reaction products. It is widely
used in the preparation of energetic materials to improve energy and temperature [5, 6]. There are many metal oxides. Wang Yi et al [7] prepared Al/Fe₂O₃ by sol-gel method and explored its reaction rate. Wang Qibui et al [8] synthesized Al/CuO with a core–shell structure via a self-assembly method: The results showed that it has good exothermic properties. Dong Haoxue et al [9] prepared Al/ NiO via a co-assembly method and studied its energy characteristics and combustion performance. Sanders [10] prepared Al/Bi₂O₃ to study the mechanism of combustion wave. Chen Jialin [11] prepared Al/MoO₃ nanocomposites via an electrospray method and studied their thermal behavior and combustion performance. Song Jiaxing et al [12] prepared Al/MnO₂ as a destructor. Experiments show that the Al/MnO₂ produces a bright flame during the reaction and penetrates the steel target easily, thus indicating that the Al/MnO₂ has good cutting performance.

MnO₂ has many different morphologies. For example, Zhou Min [13] obtained manganese dioxide nano-3D hollow nano-sea urchin structures with different crystal structures and morphologies by adjusting the temperature of the hydrothermal reaction and the concentration of ions in the solution. Its absorbing properties were then studied in detail. Nano-MnO₂ materials have structural advantages, and different structures have better electrochemical performance, which were in turn widely used in nanoscale optoelectronic devices. Subramanian et al [14] found that nanoflowers with a layered structure have a larger capacitance than nanorods with a one-dimensional tunnel structure. Wang Xun et al [15, 16] of Tsinghua University studied the redox reaction of MnO⁴⁻ and Mn²⁺. MnO₂ single crystal nanowires and nanorods with different aspect ratios were successfully prepared by adjusting the oxidant species, reactant ratio, reaction temperature, and other parameters in the hydrothermal reaction. Song Jiaxing [17] prepared a nanorod-like MnO₂ by hydrothermal synthesis, and prepared Al/MnO₂ thermite by ultrasonic mixing. The thermite prepared from rod MnO₂ has a higher exothermic rate and a lower onset temperature. There were previously many studies on the properties of single-morphological MnO₂ thermites. Researchers have conducted in-depth studies on the effects of different oxides, additive components, and different particle sizes of Al on the thermodynamics and combustion performance of Al/MnO₂ thermite [17–20]. However, the effects of different morphologies of MnO₂ on the thermite properties have not been systematically studied.

Therefore, a nanorod MnO₂ was prepared here, and two nano thermites—Al/granular MnO₂ and Al/rod MnO₂—were prepared via ultrasonic mixing. The thermite with different morphologies of manganese oxide composition was characterized and analyzed by field emission scanning electron microscope (FE-SEM), x-ray diffractometry (XRD), and differential scanning calorimeter (DSC). The light intensity test was performed in an open combustion experiment. A closed tube and a closed explosive combustion experiment were used. The combustion performance was then discussed. Finally, the results were preliminarily analyzed in terms of reaction mechanism. The objectives of this study are to figure out the changes of thermal properties and combustion behavior of nano-Al/MnO₂ thermite with different MnO₂ morphology. This study provides precise design guidance for the preparation of future thermites.

2. Experiment

2.1. Materials and reagents

A nano aluminum powder (Al) (50–80 nm) was purchased from Shanghai Naiou Nano Technology Co., Ltd Its activity was about 60%. Nanoparticle MnO₂ (50–200 nm) was purchased from Shanghai Naiou Nanotechnology Co., Ltd Potassium permanganate (KMnO₄; purity > 99.5%) was provided by Shanghai Lingfeng Chemical Reagent Co. Ltd Hydrochloric acid (HCl; mass fraction 36.0%–38.0%) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd Anhydrous ethanol (purity > 99.7%) and deionized water were purchased from Shanghai Jiuyi Chemical Reagent Co. Ltd All of the reagents were of analytical grade and used directly without further processing.

2.2. Sample synthesis and preparation

The reaction between KMnO₄ and HCl is divided into two situations. When the HCl is excessive, the reaction generation is MnCl₂, and the corresponding reaction equation is

\[
2\text{KMnO}_4 + 16\text{HCl} (\text{concentrated}) \rightarrow 2\text{KCl} + 2\text{MnCl}_2 + 8\text{HCl} + 4\text{H}_2\text{O} \tag{1}
\]

However, when the concentration of HCl is low, i.e., when KMnO₄ is excessive, the MnCl₂ produced by the previous reaction will be oxidized to MnO₂ precipitates via the corresponding reaction equation:

\[
2\text{KMnO}_4 + 3\text{MnCl}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{KCl} + 5\text{MnO}_2 \downarrow + 4\text{HCl} \tag{2}
\]
The reaction equation for the reaction of KMnO₄ and HCl to form MnO₂ is

$$2\text{KMnO}_4 + 8\text{HCl} \rightarrow 2\text{KCl} + 2\text{MnO}_2 \downarrow + 3\text{Cl}_2 \uparrow + 4\text{H}_2\text{O}$$

Song Jiaxing et al [21] prepared nanorod-like MnO₂ samples via a hydrothermal method; KMnO₄ (0.035 mol) was weighed and dissolved in deionized water. According to the stoichiometric ratio of formula (3), 4 ml of concentrated HCl (to ensure the excess of KMnO₄) was extracted with a pipette, and concentrated HCl was added to deionized water at room temperature with magnetic stirring to dilute the sample 10-fold. Diluted HCl was then added dropwise to the aqueous KMnO₄ solution. The mixed reaction solution was transferred to a 100 ml hydrothermal reactor and reacted at 140 °C for 12 h. The dark brown precipitate was obtained by centrifugation—the precipitate was washed several times with deionized water and absolute ethanol. Finally, the dark brown product was dried in a vacuum oven at 60 °C to obtain a dark brown nanorod-like MnO₂ sample.

Nano-Al/MnO₂ thermite was prepared via an ultrasonic dispersion method, and the quality of nano-MnO₂ was controlled at 120 mg. According to the stoichiometric ratio, the thermite was prepared according to the ratio in table 1. According to the calculation of the chemical equation, the mass of Al required for 120 mg of MnO₂ to reach zero oxygen equilibrium is about 49.6 mg. Considering that the activity of Al powder is about 65%, the mass of sample aluminum is 76 mg. The preparation process of sample I was taken as an example: Here, 120 mg of nanorod-like MnO₂ was dispersed in 20 ml of anhydrous ethanol; 76 mg of Al powder was then dispersed in 10 ml of absolute ethanol. The two were ultrasonically dispersed for 30 min using an ultrasonic cleaner. Two cups of the solution were mixed into the same beaker and placed in an ultrasonic cleaner to continue ultrasonic dispersion for 30 min to obtain a uniformly dispersed suspension. Finally, the dark gray nano-Al/rod MnO₂ thermite sample was obtained after the suspension was dried at 80 °C for 12 h. The preparation of nano-Al/granular MnO₂ thermite is the same as the above-mentioned process.

### 2.3. Characterization and thermal analysis

The morphological features and element distribution of the nano thermite were observed by FE-SEM (Hitachi High-Technologies Corporation, S-4800 II, Japan). The accelerating voltage of the device was 5 kV for imaging.

The phase structure of Al/MnO₂ was characterized by XRD (Bruker, D8 Advance, Germany) using Cu Kα radiation (λ = 0.1542 nm) at 20 kV.

Thermal analysis of the thermite samples was performed via DSC (NETZSCH STA 449F2, Germany). The temperature range for thermal analysis was 25 °C–800 °C, and the Ar flow was 100 ml·min⁻¹. To remove as much air as possible from the sample cell, argon flow was started for 40 min to evacuate the air before increasing the temperature. The sample mass is within 2 mg for safety. To further study the reaction kinetics, the samples were subjected to DSC tests at heating rates of 15, 20, and 25 K·min⁻¹, respectively.

### 2.4. Combustion experiment

We used a self-designed combustion experiment device for the open combustion experiment, the closed tube combustion experiment, and the constant volume combustion experiment. As show in figure 1, a thermite sample was ignited by rapidly heating a 0.1-mm-diameter nichrome wire using an adjustable DC generator. The combustion process was recorded using a high-speed camera (FASTCAM SA-Z, Japan). The sampling rate is 20,000 fps, the frame size is 768 × 768 pixels, and the aperture value is 2.2. At the same time, we used a light signal detector (THORLABS DET02ADC/M, USA) and an oscilloscope (TELEDYNE WAVESURGER3054, USA) to record the light intensity curve during the combustion process. In addition, current coils and voltage detectors are incorporated into the device to obtain current and voltage signals during ignition. The current transfer ratio of the current coil is 1 V A⁻¹, and the relationship between pressure and voltage is P = 5.63 V. The mass of the thermite sample is 10 mg; care should be taken to ensure the uniformity of the sample to eliminate the effect of density gradients.

As show in figure 2, a high-speed camera was used to measure the speed of the flame reaction front with a sampling rate of 40,000 fps, a frame size of 284 × 160 pixels, and an aperture value of 6.4. The mass of Al/MnO₂ is 15 mg. It was packed in an acrylic tube with an inner diameter of 2 mm and a length of 20 cm, but the charge

### Table 1. Details of the main exothermic peaks of the thermite.

| Sample       | Corresponding peak | Initial reaction temperature (°C) | Heat release (J·mol⁻¹) | Total heat release (J·mol⁻¹) |
|--------------|--------------------|----------------------------------|-----------------------|----------------------------|
| Al/granule MnO₂ | A                  | 230                              | —                     | 981.81                    |
|              | B                  | 419.7                            | 69.35                 |                            |
|              | C                  | 550                              | 912.46                |                            |
|              | D                  | 660                              | —                     |                            |
| Al/rod MnO₂   | E                  | 230                              | —                     | 1274.39                   |
|              | F                  | 567.39                           | 1274.39               |                            |
loading is only 2.0 cm. The actual load density was calculated as the load mass (15 mg) divided by the load volume (62.8 mm$^3$), which resulted in 0.229 g·cm$^{-2}$.

As shown in figure 3, a self-made closed detonator was used to ignite the thermite sample in the closed detonator using an open combustion design. The work also used a pressure sensor (PCB), a signal conditioner (TELEDYNE MODEL 482C SERIES; USA), and an oscilloscope (TELEDYNE WAVESURGER3054; USA) to record the pressure change in the closed explosive device. The mass of the thermite sample is 10 mg, and care should be taken to ensure the uniformity of the sample to eliminate the effect of density gradients.

3. Results and discussion

3.1. Morphology and crystal form analysis

Figure 4 shows the microstructures of the two MnO$_2$ samples as observed by FE-SEM. Figure 4(a) shows that commercial MnO$_2$ has a diameter of 50–200 nm; it is irregular in granularity and exhibits dense packing. The
synthesized MnO₂ particles are rod-shaped with diameters ranging from 80 to 200 nm and lengths of 2 to 5 μm. Figure 4(b) shows that the rod-shaped MnO₂ particles are uniformly dispersed with a smooth surface; the dispersibility is much better than that of granular MnO₂.

The two thermites prepared by ultrasonic mixing were analyzed by XRD to determine the crystal forms of the samples. Figure 5 shows XRD results of the Al/granular MnO₂ thermite sample and the Al/rod MnO₂ thermite sample as blue and green curves, respectively. Both curves contain diffraction characteristic peaks of Al (black vertical solid lines). A standard PDF card (Al JCPDS 85–1327) shows that the Al nanoparticles should have a lattice constant of \( a = b = c = 4.049 \text{ Å} \) and a space group of Fm-3 m (225). The corresponding degrees of 2θ are 38.5°, 44.7°, 65.1°, and 78.2°. Both curves contain diffraction characteristic peaks of MnO₂ marked by a red vertical solid line; this nicely matches the standard PDF card (ICDD/JCPDS 44–0141 MDI Jade 6.0). XRD results show that the morphology of rod-like MnO₂ prepared by the hydrothermal method is different than a commercial granular MnO₂, but it belongs to the same crystal form—both are \( \alpha \)-MnO₂. The purity and composition consistency of the two thermite samples prepared by the ultrasonic mixing method were relatively high and are the basis for subsequent research.

Figure 6 shows Al and MnO₂ are uniformly mixed and dense. Al is in direct contact with MnO₂ with a low density. Some Al particles are attached to the surface of rod-shaped MnO₂. Part of the Al powder agglomerates and adversely affects the exotherm and ignition [17], but most of the Al powder is uniformly dispersed. The mapping images better illustrate the uniformity of the sample's dispersion.
3.2. Thermal analysis

The thermal properties of the thermite samples were tested by DSC, and the results are shown in figure 7. Specific information on the main exothermic peaks of the thermite samples is listed in table 1.

Figure 7(a) shows two exothermic peaks and a weak endothermic peak. The exothermic peak is not sharp, the ignition temperature of the main exothermic peak is 550 °C, and the total exothermic heat is 981.81 J mol⁻¹. Figure 7(b) has a weak endothermic peak near 230 °C, which may be due to the evaporation of adsorbed water, structural water, solvent, or impurities on its surface during the preparation of thermite [22]. The exothermic peak is sharp and obvious. The ignition temperature is 567.39 °C, and the exotherm is 1274.39 J mol⁻¹. The DSC analysis showed that the aluminothermic reaction occurred from 400 °C to 700 °C. The thermal properties
of the two nano thermites are significantly different. The change of the morphology of Al/rod MnO₂ brings about a delay in the ignition temperature and an increase in heat release.

The first difference appears around 450 °C with a small exothermic peak for the Al/granular MnO₂. This may be due to the high density of the sample shown in figure 6(a), thus forming a thermal insulation layer between Al and granular MnO₂ in the inner layer. The outer layer sample first produces an exothermic reaction around 450 °C. However, there are voids in the Al/rod-MnO₂ so that the entire sample is heated evenly and almost simultaneously produces an exothermic reaction with only one main exothermic peak.

The second difference occurs around 550 °C. The main exothermic peak of Al/rod MnO₂ appears before Al/rod MnO₂, and the reaction onset temperature of Al/rod MnO₂ is 550 °C, which is earlier than that of Al/rod-like MnO₂. The voids between the rod-like MnO₂ lead to fewer contact points between the nano-Al particles and their surfaces. In contrast, the mixing density of Al/rod MnO₂ is larger, which provides more surface contact points, which is conducive to the rapid formation of ‘hot spots.’ The exothermic reaction of Al and granular MnO₂ at the periphery of the sample around 450 °C is also in advance of the initial reaction temperature and creates the appropriate reaction conditions.

The exotherm of Al/rod MnO₂ is higher than that of Al/rod MnO₂. In the Al/rod MnO₂, the higher density of granular MnO₂ restricts the flow of Al nanoparticles and cannot fully realize the release of thermal properties. This may explain the difference in thermal release. The voids between the oxides also enable the free flow of hot reactive gases between the separated nano-Al particles [23]. The surface of rod-shaped MnO₂ provides conditions for dispersing Al particles as well as the splashed Al accelerates the reaction with rod-shaped MnO₂, which effectively increases the reaction rate and heat release. A schematic diagram of the thermal reaction mechanism of the thermite is shown in figure 8.

The third difference appears around 660 °C near the melting point of Al. Al/rod MnO₂ had a weak endothermic peak signal around 660 °C indicating that some nano-Al powders failed to participate in the aluminothermic reaction and remained in excess. This may be due to agglomeration and/or incomplete distribution. The phenomenon of agglomeration may lead to delayed or even incomplete reaction, which may explain the weak endothermic signal. In addition, the local uneven distribution caused by the ultrasonic dispersion method will affect the test results due to the small quality of the DSC test.

### 3.3. Non-isothermal thermodynamic analysis

Here, the Kissinger–Akahira–Sunose (KAS) method [24] was used to analyze the DSC measurement data and calculate the activation energy (Eₐ) of the sample. The basic formula is

\[
\ln \left( \frac{\beta}{T_P^2} \right) = - \frac{E_a}{RT_P} + \ln \frac{AR}{E_a}
\]

Term A is the pre-exponential factor (s⁻¹), R is the universal gas constant (8.214 J·mol⁻¹·K⁻¹), Tₚ is the DSC peak temperature (K), and β is the linear heating rate (K·min⁻¹). Assuming the same conversion of the samples at the peak temperature, the relationship between \( \ln \left( \frac{\beta}{T_P^2} \right) \) and \( \frac{1}{T} \) is a straight line whose slope can be converted to the Eₐ value. Table 2 specifically lists the calculation parameters of the thermal reaction Eₐ of the samples. Figure 9 shows multiple-rate scanning images of the two samples and a linear fitting diagram of the test peak temperature point.
The activation energy of Al/rod-like MnO₂ is 234.36 kJ·mol⁻¹, and the fitting equation is \( y = -28188.73x + 21.39 \). The activation energy of Al/ granular MnO₂ is 187.83 kJ·mol⁻¹, and the fitting equation is \( y = -27808.6x + 20.97 \). A higher activation energy makes it more difficult for the reaction to occur, which corresponds to a delay in the ignition temperature of Al/rod MnO₂ in the DSC curve. Similarly, the temperature peaks all move backward with increasing heating rate. This result indicates that the thermal explosion critical
The temperature of the Al/rod-shaped MnO₂ is higher. It is difficult to change from thermal decomposition or combustion to explosion—this makes the system safer.

### 3.4. Burning test

Figure 10 is a high-speed photograph of an open combustion experimental flame. The burning time of Al/rod MnO₂ is 120 ms, the flame is jet-like, and sparks are sputtered around. The burning time of Al/rod MnO₂ is 30 ms, the flame area is large, and the burning speed is fast. Figure 11 shows the light intensity test results of the open combustion experiment indicating light intensity signal curves of the two samples when they are openly burned. The mass of the samples used is 10 mg. The instantaneous increase in the light intensity signal indicates that the ignition excitation is rapid, and the peak light intensity of the two groups of samples is not significantly different; the duration of the light intensity signal is quite different, however. The light intensity existence time of Al/rod MnO₂ is 0.0146 s, and the light intensity existence time of Al/rod MnO₂ is 0.0146 s. This shows that the combustion rate of Al/rod MnO₂ is much faster than that of Al/rod MnO₂.

Figure 12 is a high-speed photograph of a closed-tube combustion experiment. The images were combined at certain time intervals to visually display the propagation process of the combustion flame within a certain time range. The results show that the Al/rod MnO₂ cannot self-propagate the combustion in a closed tube. The flame wave propagates rapidly after the Al/rod MnO₂ is ignited and excited. The propagation distance of the combustion wave with time is recorded in table 3. The propagation distance and velocity curves are shown in figure 13.
Figure 11. Light intensity test curve of sample heated with wire ignition and combustion.

Figure 12. High-speed photograph of the sample burning in the combustion tube. (a) Al/granule MnO₂ thermite and (b) Al/rod MnO₂ thermite.

Table 3. Specific data of sample combustion.

| Reactant       | Time (μs) | Length (cm) | R²     | Maximum speed (m·s⁻¹) |
|----------------|-----------|-------------|--------|-----------------------|
| Al/rod MnO₂    | 0         | 0           | 0.98513| 339.60                |
| 50             | 0.2       |             |        |                       |
| 100            | 1.8       |             |        |                       |
| 150            | 2.0       |             |        |                       |
| 200            | 3.8       |             |        |                       |
| 250            | 7.0       |             |        |                       |
| 300            | 9.0       |             |        |                       |
| 350            | 10.4      |             |        |                       |
| 400            | 12.0      |             |        |                       |
| 450            | 12.2      |             |        |                       |
| 500            | 13.0      |             |        |                       |
| 550            | 14        |             |        |                       |
| 600            | 15.5      |             |        |                       |
| 650            | 16.0      |             |        |                       |
Figure 13 shows the combustion wave propagation velocity of Al/rod MnO₂ thermite first increases and then decreases. Its maximum propagation velocity reaches 339.6 m·s⁻¹. It takes a certain time to reach the maximum velocity during the propagation of the combustion wave, and the load density of the thermite sample in the middle pipe section is very low; the convective gas can move forward with less resistance [20]. Therefore, the speed of the burn wave will increase in the middle section.

Interestingly, in the open combustion experiment, the two stacked samples exhibited no substantial difference in their combustion behavior. However, the micro-channel environment did not lead to self-propagating combustion of Al/ granular MnO₂; the Al/rod MnO₂ has better combustion performance.

The convective propagation mechanism is believed to be the dominant principle in the combustion of the thermite in a closed tube. The convective gas produced by the exothermic reaction pushes the reaction medium forward at a very fast speed, thus transferring heat by convection [25].

In thermite composed of granular MnO₂, the higher density of granular MnO₂ leads to smaller voids between oxides, which restricts the free flow of hot reaction gas between Al particles. In contrast, the distribution of components is not uniform in some parts when the sample is prepared by ultrasonic dispersion method; the quality of the test sample is small. This comprehensively results in a Al/ granular MnO₂ thermite sample that cannot fully release its thermal properties and cannot self-propagate. A schematic diagram of the thermal reaction mechanism of the thermite is shown in figure 14. In contrast, the rod-like MnO₂ with a high aspect ratio is cross-connected, and the oxide has more voids. Al is released from the heated alumina layer and is transferred along a favorable energy direction by thermal reaction gas diffusion. This increases the burning rate.

Figure 13 shows the combustion wave propagation velocity of Al/rod MnO₂ thermite first increases and then decreases. Its maximum propagation velocity reaches 339.6 m·s⁻¹. It takes a certain time to reach the maximum velocity during the propagation of the combustion wave, and the load density of the thermite sample in the middle pipe section is very low; the convective gas can move forward with less resistance [20]. Therefore, the speed of the burn wave will increase in the middle section.

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Figure 15 shows pressure test results of a constant volume combustion experiment. The mass of the samples used here is 15 mg. The difference in the results were obvious, which indicates that the rod-shaped MnO₂ has better gas production performance. Judging from the duration of the pressure peak, the Al/ granular MnO₂ has a
slow burning speed while the Al/rod MnO₂ has a faster burning speed. This again confirms the conclusions of the open combustion experiment and the closed tube combustion experiment.

4. Conclusion

DSC analysis shows that the thermal decomposition performance and safety performance of Al/rod MnO₂ are better than Al/granular MnO₂. The exothermic heat of Al/rod MnO₂ is 1274.39 J·mol⁻¹, which is much larger than Al/granular MnO₂ of 981.81 J·mol⁻¹. The initial reaction temperature of the Al/rod MnO₂ is 567.39 °C, which is 17.39 °C later than the 550 °C of Al/granular MnO₂.

Non-isothermal thermodynamic analysis showed that the activation energy of Al/rod MnO₂ is 234.36 kJ·mol⁻¹, which is higher than that of Al/granular MnO₂ (187.83 kJ·mol⁻¹). This indicates that it is safer.

Both thermites were successfully ignited with dazzling lights and harsh explosions in open combustion experiments. The burning time of Al/rod MnO₂ is significantly shorter than that of Al/granular MnO₂, and the flame area is larger. In addition, there is a big difference in the duration of the burning light intensity signal between the two. This indicates that the burning rate of Al/rod MnO₂ is much faster than Al/granular MnO₂.

The combustion behavior is significantly different in the closed-tube combustion experiment. Al/granular MnO₂ cannot self-propagate combustion in a closed tube. The Al/rod MnO₂ rapidly ignited, propagated, and burned. The propagation velocity of the combustion wave first increased and then decreased, and its maximum propagation velocity reached 339.6 m·s⁻¹. The results show that the combustion performance of Al/rod MnO₂ is more advantageous in the micro-channel environment.

A constant volume combustion experiment showed that the pressure peak of the Al/rod MnO₂ thermite sample is 0.938 Mpa, which is almost two-fold the pressure peak of the Al/granular MnO₂ thermite sample. This shows that the rod-shaped MnO₂ gas production performance is better. The duration of the pressure peak indicates that the Al/rod MnO₂ thermite sample burns faster. This confirms the conclusions of the open combustion experiment and the closed tube combustion experiment. In conclusion, the thermal performance and combustion performance of Al/rod MnO₂ are better than Al/granular MnO₂; the Al/rod MnO₂ is safer.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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