Thermal Decomposition and Thermal Reaction Process of PTFE/Al/MnO₂ Fluorinated Thermite

Jun Zhang®, Junyi Huang®, Xiang Fang *, Yuchun Li *, Zhongshen Yu, Zhenru Gao, Shuangzhang Wu, Li Yang, Jiaxiang Wu and Jiaying Kui

College of Field Engineering, PLA Army Engineering University, Nanjing 210001, China; zhangjun11067318@163.com (J.Z.); huangjunyi357@163.com (J.H.); 13390924860@163.com (Z.Y.); gygzt@sina.com (Z.G.); wushzh4394@126.com (S.W.); speedinessli@163.com (L.Y.); wujiaxiang1356@163.com (J.W.); xxkk6993@163.com (J.K.)
* Correspondence: fangxiang3579@163.com (X.F.); liyuchunmail@163.com (Y.L.);
Tel.: +86-15651958735 (X.F.); +86-25-8082-1320 (Y.L.)

Received: 15 November 2018; Accepted: 29 November 2018; Published: 3 December 2018

Abstract: To better understand the thermal decomposition and reaction process of a fluorine-containing powdery thermite, PTFE/Al/MnO₂, reactions at different temperatures were investigated by the TG/DSC-MS technique. The corresponding reaction products were characterized with XRD phase analysis. Another three thermite materials, i.e., PTFE/Al, Al/MnO₂, and PTFE/MnO₂, were also prepared for comparison. Results showed that PTFE behaved as both oxidizer and reducer in PTFE/Al/MnO₂ fluorinated thermite. The thermal decomposition and reaction process of as-fabricated ternary thermite could be divided into two stages—the mutual reaction between each of PTFE, Al, and MnO₂ and the subsequent reaction produced between Al and Mn3O4/MnF2. Compared with the three control systems, the specially designed ternary system possessed a shorter reaction time, a faster energy release rate, and a better heat release performance.

Keywords: fluorine-containing thermite; PTFE/Al/MnO₂; thermal decomposition; TG/DSC-MS; XRD

1. Introduction

Reactive materials can explode, deflagrate, and release a huge amount of chemical energy under impact. A typical representative of reactive materials [1], thermite features high energy, high density, flexible formulation, and a high adiabatic temperature. Conventional aluminothermic agents commonly comprise Al as the fuel and metal oxides (Fe₂O₃, MoO₃, CuO, Bi₂O₃, MnO₂, etc.) as the oxidant. However, the limited extent of a combination between an oxidant and a reductant can result in a low reaction rate, a smaller amount of actual heat release, an unconcentrated reaction process, a high initial temperature (>900 °C), a low energy release rate, and a compromised mechanical strength [2].

Research on fluorine-containing aluminothermic agents has received extensive attention recently. Due to a strong elemental electronegativity, fluorine atoms tend to lose the outermost electrons and become highly oxidizing. Polytetrafluoroethylene (PTFE) is a commercial fluorine-containing polymer [3–6] with a fluorine content of 76 wt.% [7]. For traditional oxide-based aluminothermic agents, Al and oxides react mostly in a condensed phase, whereas the addition of PTFE as a binder can trigger a redox reaction between PTFE and Al to yield AlF₃. Studying the application of fluorinated polymers in thermite, Li [8] found that the low boiling point of AlF₃ could prevent it from covering the Al particle surface and hindering the reaction. Puts and Crouse [9] investigated the effect of metal fluoride on PTFE decomposition, concluding that the catalytic effect of AlF₃ could accelerate the reaction process and further promote the decomposition by inducing a 30 °C drop for the reaction.
temperature. In the meantime, the promotion effects exerted by PTFE were also reported for the thermal reaction, including a faster energy release, a higher flame temperature, and a greater reaction pressure of the thermite [10–13]. The addition of PTFE as a binder or matrix can magnify the original advantages, e.g., a high energy density and a high adiabatic temperature, and improve the mechanical strength of conventional powdered aluminothermic agents; the reaction materials will exhibit a better energy release as well. Furthermore, an as-fabricated damage element outperforms the inert one with its flexible formula, high oxygen carrying capacity, impact-based initiation, and its capability of generating a large number of elemental C (carbon) short circuit electronic components. At present, the research focus has been gradually shifting from thermal decomposition and reaction processes in traditional studies to the combustion performance of fluorine-containing thermites [5,14].

In this work, PTFE/Al/MnO$_2$, a powdery fluorinated aluminothermic agent, was successfully fabricated by referring to the traditional aluminum heat agent and adding PTFE as a binder or matrix. Meanwhile, PTFE/Al, Al/MnO$_2$, and PTFE/MnO$_2$ were also prepared for comparison. Thermogravimetric (TG) analysis, differential scanning calorimetry (DSC), and mass spectrometry (MS) were used to analyze the reaction processes at different temperatures, while X-ray diffraction (XRD) was employed for the residue characterization. This study aims at providing practical guidance for the fluorination treatment of traditional thermites.

2. Experimental Section

2.1. Sample Preparation

PTFE (average particle size of 25 µm) was purchased from Shanghai 3F New Materials Co., Ltd. (Shanghai, China), Al powder (average particle size of 1–2 µm) was provided by Jintian Aluminum High-Tech Co., Ltd. (Luxi, Hunan, China) and MnO$_2$ powder (average particle size of 3–5 µm) were commercially available at Europe Nano Technology Co., Ltd. (Shanghai, China). The formulations of the four materials prepared, i.e., PTFE/Al, Al/MnO$_2$, PTFE/MnO$_2$, and PTFE/Al/MnO$_2$, are listed in Table 1.

| Sample Composition (wt.%) | PTFE | Al | MnO$_2$ |
|--------------------------|------|----|---------|
| Al/MnO$_2$               | \   | 30 | 70      |
| PTFE/Al                  | 51   | 49 | \       |
| PTFE/MnO$_2$             | 42   | \  | 58      |
| PTFE/Al/MnO$_2$          | 30   | 29 | 41      |

The samples were prepared with the following procedure. First, the powder of various raw materials was added to a beaker at a designated ratio, followed by the addition of an appropriate amount of ethanol absolute. After the initial dispersion via 20 min stirring, the beaker was transferred into an ultrasonic system and kept for 30 min. The water bath was refreshed every 5 min during ultrasonication to prevent the solution from overheating and further triggering the reaction. The samples obtained were then dried in a vacuum oven at 60 °C for 48 h. Finally, the dried powder was sieved to produce uniform powdery materials.

2.2. Experimental Process

A combined testing system of thermogravimetry-differential scanning calorimetry (TG-DSC, NETZSCH-STA449C, NETZSCH, Bavaria, Germany) and mass spectrometry (MS, NETZSCH-QMS403C, NETZSCH, Bavaria, Germany) served as the primary analytical method for thermal decomposition and reaction processes of the four samples. Gas products were introduced into the mass spectrometer through a capillary tube, and their composition changes were monitored and recorded at different
temperatures from 25 °C to 1000 °C with a fixed heating rate of 10 °C/min. To prevent air from participating in the reaction, experiments were carried out in a highly pure argon atmosphere with argon purging at 30 mL/min. Meanwhile, the capillary temperature was set at 200 °C to avoid gases cooling down within the capillary tube. The solid residues thermally analyzed at different temperatures were recovered and their phase composition was characterized with X-ray diffraction (XRD, Bruker D8 ADVANCE, Bruker, Berlin, Germany). The samples were scanned from 5° to 90° (2θ) at a scan step of 0.02°.

3. Results and Discussion

To develop a better understanding of the specific processes for the thermal decomposition and the reaction of PTFE/Al/MnO2 powdery thermite, the reaction processes of PTFE/Al, Al/MnO2, and PTFE/MnO2 at different temperatures should be analyzed in advance.

3.1. Thermal Decomposition and Thermal Reaction Processes of PTFE/Al

The TG-DSC curves recorded for the PTFE/Al thermal decomposition are depicted in Figure 1, in which a total of five peaks can be observed on the DSC curve. Peak A covers a temperature range from 323.2 °C to 358.1 °C, where no change shows up on the TG curve; it stands for the melting endotherm of PTFE (PTFE shows a melting point at 327 °C [15]). The TG curve suggests that the sample weight dropped sharply from 509 °C; meanwhile, C2F4+ ions (m/z = 100, Figure 2) were detected by mass spectrometry. Thus, peak B appearing then on the DSC curve should result from the endothermic decomposition of PTFE with C2F4 as the primary decomposition product. As for peak C, which begins at 597.9 °C and ends at 607 °C, it is attributed to the exothermic reaction between micron Al and PTFE decomposition products [3] that yielded AlF3 and C (carbon). Peaks B and C are actually the superimposed results of the endothermic PTFE decomposition and the exothermic PTFE/Al reaction. According to the MS spectrum presented in Figure 2, C2F4+ was produced and accumulated at 513 °C and then largely depleted due to its reaction with Al. However, since more AlF3 were produced, a mounting catalytic effect on PTFE decomposition [9] was exerted, which raised the C2F4+ content again to the peak value of 574 °C. As the PTFE decomposition ended at 619 °C, the content of C2F4 reduced gradually to zero (Figure 2). Furthermore, the excessive Al melted at about 660 °C, which gave rise to the endothermic peak D on the DSC curve.

![Figure 1. Thermogravimetry-differential scanning calorimetry (TG-DSC) curve of the PTFE/Al (polytetrafluoroethylene/aluminum) sample.](image)
At about 780 °C, the TG curve shows a second decline with a mass loss of 2.21 wt.%, and the endothermic peak E appears on the DSC curve correspondingly. The sample composition then was supposed to be C (carbon black), AlF$_3$, and excess Al, and the endothermic sublimation of AlF$_3$ might account for the appearance of peak E. The TG-DSC curve recorded for the heating of neat AlF$_3$ up to 1200 °C under the same conditions is further provided in Figure 3 for verification. As can be seen, AlF$_3$ sublimation gave rise to a remarkable drop at 832 °C on the TG curve, accompanied with an endothermic peak B on the DSC curve. Therefore, peak E in Figure 1 should also be attributed to AlF$_3$ sublimation at high temperature. The only difference was that the sublimation temperature of AlF$_3$ in the PTFE/Al sample was 50 °C lower than that of the neat AlF$_3$.

The products of the PTFE/Al reaction at different temperatures were further characterized with the XRD phase analysis. The XRD patterns are depicted in Figure 4, while the product composition is listed in Table 2. The results indicate that Al$_4$C$_3$ was synthesized from C and excess Al at high temperatures.
with Al preferentially. Al₂O₃, as a product, could not be detected by XRD due to its amorphous state or poor crystallinity [19]. Therefore, peaks A and B on the DSC curve were caused by the superposition of MnO. A great amount of Al and Mn in the reaction products point out that the product components were Al, Mn₂O₃, and MnO, but without Mn₃O₄ (Figure 6). According to the process of MnO₂ decomposition, MnO should not be included as a product. Hence, the generation of the oxides of high-valence Mn by Al might account for the generation of MnO. A great amount of Al and Mn₃O₄ were left after the reaction was completed, which further proved that MnO was produced by Al reacting with Mn₂O₃.

Table 2. Product composition in different temperature ranges during PTFE/Al (polytetrafluoroethylene/aluminum) thermal reactions.

| Temperature/°C | Products                  |
|---------------|---------------------------|
| <450          | PTFE and Al, AlF₃, C, and C₂F₄ (g) |
| 450–590       | Al, AlF₃, Al₄C₃, and C₂F₄ (g) |
| 590–619       | Al, AlF₃, Al₄C₃, and Al₄C₃ |
| 619–1000      | Al, AlF₃, and Al₄C₃         |

3.2. Thermal Decomposition and Thermal Reaction Process of Al/MnO₂

Figure 5 presents the TG-DSC curves for the Al/MnO₂ (30/70, w/w) thermal decomposition. MnO₂ is chemically unstable and can decompose easily [16]. The two degradation stages on the TG curve correspond to the two-step decomposition process of MnO₂ [17,18]. However, the appearance of two exothermic peaks, A and B, indicates that exothermic reactions still existed during the whole reaction process, and Figure 6b further suggests that the product consisted of Al, Mn₂O₃, and Mn₃O₄ after the reactions ending at 620 °C. Given that Mn₂O₃ decomposes into Mn₃O₄ at a temperature higher than 620 °C, the generation of Mn₃O₄ accompanied by heat release should be attributed to the reaction between Al and some MnO₂—MnO₂ has a stronger oxidizability than Mn₂O₃ and would react with Al preferentially. Al₂O₃, as a product, could not be detected by XRD due to its amorphous state or poor crystallinity [19]. Therefore, peaks A and B on the DSC curve were caused by the superposition of the Al/MnO₂ reaction exotherm and the MnO₂ decomposition endotherm. Moreover, peak C is assigned to the melting endotherm of excessive Al.

Peak D appearing later implies the existence of an exothermic reaction during the Mn₂O₃ decomposition, which ended as the temperature rose to about 800 °C. Meanwhile, the XRD patterns of the reaction products point out that the product components were Al, Mn₃O₄, and MnO, but without Mn₂O₃ (Figure 6). According to the process of MnO₂ decomposition, MnO should not be included as a product. Hence, the reduction of the oxides of high-valence Mn by Al might account for the generation of MnO. A great amount of Al and Mn₃O₄ were left after the reaction was completed, which further proved that MnO was produced by Al reacting with Mn₂O₃.

\[
\begin{array}{cccccc}
\text{Temperature/°C} & \text{<450} & \text{450–590} & \text{590–619} & \text{619–1000} \\
\hline
\text{Products} & \text{PTFE and Al} & \text{Al, AlF₃, C, and C₂F₄ (g)} & \text{Al, AlF₃, Al₄C₃, and C₂F₄ (g)} & \text{Al, AlF₃, and Al₄C₃} \\
\end{array}
\]
Figure 5. TG-DSC curve of Al/MnO\(_2\).

Figure 6. XRD patterns of Al/MnO\(_2\) solid residues at different temperatures. (a) XRD patterns at 450 °C; (b) XRD patterns at 620 °C; (c) XRD patterns at 800 °C; (d) XRD patterns at 1000 °C; (e) XRD patterns at 1200 °C.

1 Al    2 MnO\(_2\)   3 Mn\(_2\)O\(_3\)    4 Mn\(_3\)O\(_4\)    5 MnO    6 Mn    7 Al\(_2\)O\(_3\)    8 MnAl\(_2\)O\(_4\)
which suggests that Al$_2$O$_3$, Mn, MnAl$_2$O$_4$, and MnO existed as the product components while Al and Mn$_3$O$_4$ were not contained. As can be inferred, Mn and MnAl$_2$O$_4$ were formed during the exothermic reaction between Al and Mn$_3$O$_4$. Since Mn$_3$O$_4$ possesses a stronger oxidizability than MnO does, Al reacted with Mn$_3$O$_4$ preferentially. As for Al$_2$O$_3$, on the one hand, the reaction between MnO$_2$ and Al would generate amorphous Al$_2$O$_3$, which further transformed into crystalline Al$_2$O$_3$ with a faster nucleation process at a higher temperature; on the other hand, the possible reaction between Al and Mn$_3$O$_4$ would also produce Al$_2$O$_3$ along with Mn.

3.3. Thermal Decomposition and Thermal Reaction Process of PTFE/MnO$_2$

TG-DSC curves corresponding to the thermal decomposition of PTFE/MnO$_2$ (42/58, w/w) are given in Figure 7. As discussed above in Sections 3.1 and 3.2, peak A stands for the melting endotherm, peak B for the decomposition endotherm of PTFE and MnO$_2$, and peak D for the decomposition endotherm of Mn$_2$O$_3$.

Figure 6d is the pattern recorded at the end of the reaction represented by peak E (1000 °C), which suggests that Al$_2$O$_3$, Mn, MnAl$_2$O$_4$, and MnO existed as the product components while Al and Mn$_3$O$_4$ were not contained. As can be inferred, Mn and MnAl$_2$O$_4$ were formed during the exothermic reaction between Al and Mn$_3$O$_4$. Since Mn$_3$O$_4$ possesses a stronger oxidizability than MnO does, Al reacted with Mn$_3$O$_4$ preferentially. As for Al$_2$O$_3$, on the one hand, the reaction between MnO$_2$ and Al would generate amorphous Al$_2$O$_3$, which further transformed into crystalline Al$_2$O$_3$ with a faster nucleation process at a higher temperature; on the other hand, the possible reaction between Al and Mn$_3$O$_4$ would also produce Al$_2$O$_3$ along with Mn.

The TG curve suggests a 41.3% decrease in the sample weight as the temperature rose from 470 °C to 580 °C. Theoretically, the weight loss should equal 47.34 wt.% if PTFE and MnO$_2$ decomposed independently without any reaction happening between them. Thus, there might be an exothermic reaction between C$_2$F$_4$ and MnO$_2$ (or Mn$_2$O$_3$), which gave rise to peak C on the DSC curve. The reaction mechanism is speculated as Formulas (1) and (2).

$$C_2F_4 + 2MnO_2 \rightarrow 2CO_2 + 2MnF_2$$  \hspace{1cm} (1)

$$2C_2F_4 + 2Mn_2O_3 \rightarrow 4MnF_2 + 3CO_2 + C$$  \hspace{1cm} (2)

During the reaction process of PTFE/Al/MnO$_2$ samples, the amount of CO$_2$ produced peaked at 573 °C (Figure 8a), and the formation of MnF$_2$ was also detected (Figure 9b). With a slight endothermic peak (peak E of Figure 7) observed near 856 °C—the melting point of MnF$_2$, the inclusion of CO$_2$ and MnF$_2$ in reaction products was thus confirmed. This further proves the occurrence of an exothermic reaction between PTFE and MnO$_2$ (or Mn$_2$O$_3$). However, since this reaction coincided with the MnO$_2$ decomposition, it is difficult to determine whether MnO$_2$ or Mn$_2$O$_3$ was involved in the reaction.
During the reaction process of PTFE/Al/MnO2 samples, the amount of CO2 produced peaked at 573 °C (Figure 8a), and the formation of MnF2 was also detected (Figure 9b). With a slight endothermic peak (peak E of Figure 7) observed near 856 °C—the melting point of MnF2, the inclusion of CO2 and MnF2 in reaction products was thus confirmed. This further proves the occurrence of an exothermic reaction between PTFE and MnO2 (or Mn2O3). However, since this reaction coincided with the MnO2 decomposition, it is difficult to determine whether MnO2 or Mn2O3 was involved in the reaction.

Figure 8. MS spectra of gaseous products from PTFE/Al/MnO2 samples. (a) MS spectra of C2F4+; (b) MS spectra of CO2+.

Figure 9. XRD patterns of PTFE/Al/MnO2 solid residues at different temperatures. (a) XRD patterns at 450 °C; (b) XRD patterns at 650 °C; (c) XRD patterns at 800 °C; (d) XRD patterns at 1000 °C.

The TG curve starts to decline sharply at 470 °C, while peak B on the DSC curve, which is an endothermic one, starts at 515 °C. As the decomposition temperatures of MnO2 and PTFE are around 530 °C and 514 °C, respectively, the weight loss between 470 °C and 515 °C should not be attributed to
PTFE or MnO₂ decomposition. Instead, it might result from the condensation reaction between PTFE and MnO₂, as described by Formula (3).

\[(C_2F_4)_n + 2nMnO_2 \rightarrow 2nCO_2 + 2nMnF_2\]  

(3)

At temperatures higher than 580 °C, both TG and DSC curves exhibit a downward trend. It is possible that the reaction between C₂F₄ and Mn₂O₃ pushed forward the decomposition of Mn₂O₃. Then, the solid residue after DSC analysis was subjected to XRD tests. Figure 10 shows the diffraction peaks only for Mn₃O₄, while no MnF₂ has been detected. As merely about 5 mg of residue was left after DSC analysis, this ultralow content might account for MnF₂ not being found.

![XRD map of PTFE/MnO₂ after reaction.](image)

**Figure 10.** XRD map of PTFE/MnO₂ after reaction.

3.4. Thermal Decomposition and Thermal Reaction Process of PTFE/Al/MnO₂

Figure 11 demonstrates the TG-DSC curve for the PTFE/Al/MnO₂ thermal decomposition. Same as that analyzed in Section 3.3, peaks A and B are endotherms due to PTFE melting and PTFE/MnO₂ decomposition, respectively, while peak C results from the exothermic reaction between C₂F₄ and Mn oxides. Further, the mass spectrometric analysis of the gas evolution points out that CO₂⁺ was formed at 475 °C without C₂F₄⁺ (Figure 8), so the weight loss suggested by the TG thermogram from 475 °C to 515 °C was indeed attributed to the condensation reaction of PTFE with MnO₂.

The exothermic peak D covers a temperature range from 592 °C to 635 °C. As mentioned before, the exothermic reaction between Al and C₂F₄ in the PTFE/Al sample happened at 597–619 °C (Figure 1), and the one between Al and MnO₂ in Al/MnO₂ sample proceeded at 590–639 °C (Figure 5). Together with the XRD analyses in Figure 9b, which suggested that the reaction products of PTFE/Al/MnO₂ sample comprised Al, Mn₂O₃, Mn₃O₄, MnF₂, and AlF₃ at 650 °C, peak D was considered to result from the superposition reactions of Al with C₂F₄ and MnO₂.

Moreover, an exothermic peak F appears on the DSC curve from 714 °C (Figure 11), which is exactly the temperature range that corresponds to the exothermic peak D in Figure 5. Thus, there should be a certain correlation between these two exothermic reactions occurring individually in PTFE/Al/MnO₂ and Al/MnO₂. However, a drop on the TG curve for the Al/MnO₂ sample is observed in the temperature interval that stands for Mn₂O₃ decomposition, while no apparent change can be detected for the PTFE/Al/MnO₂ sample weight. Then, the XRD analysis of the corresponding reaction products was performed (Figure 9c), which demonstrates the presence of AlF₃, Mn, Al₂O₃,
and MnAl₂O₄ but the absence of Al, Mn₂O₃, Mn₃O₄, and MnF₂. Therefore, peak F should be caused by the aluminothermic reaction between Al and Mn₂O₃/Mn₃O₄/MnF₂. The newly generated products in this process were Mn, Al₂O₃, and MnAl₂O₄. This is consistent with the ones formed during the exothermic reaction of the Al/MnO₂ sample between 880 °C and 987 °C. Besides, no more exothermic peaks can be found for the PTFE/Al/MnO₂ sample in this temperature range, probably because the aluminothermic reaction before was much too intense and the enhanced exotherm reaction occurred in advance. Consequently, the exothermic reaction corresponding to peak F in the PTFE/Al/MnO₂ sample equated to the combined reactions corresponding to peaks D and E in the Al/MnO₂ samples. Furthermore, the TG curve shows no significant change between 714 °C and 783 °C. This may be owing to the limited generation of oxygen, as the fierce reaction made Mn₂O₃ reduced by Al once decomposed or even not decomposed yet.

The specific reaction process of the PTFE/Al/MnO₂ sample between 714 °C and 783 °C could not be completely determined by simply analyzing the reaction products. Since both Mn₂O₃ and Mn₃O₄ may react with Al, MnOₓ is used as an overall symbolization for Mn oxides (Mn₂O₃ and Mn₃O₄). The possible chemical reaction is described below:

\[ \text{Al} + \text{MnO}_x \rightarrow \text{Al}_2\text{O}_3 + \text{MnAl}_2\text{O}_4 + \text{Mn} \]  

Finally, the TG-DSC curves show a slight endothermic peak H between 870 °C and 910 °C accompanied with a decrease in the sample weight of 4.78 wt.%. Meanwhile, the XRD pattern in Figure 9d indicates Mn, Al₂O₃, and MnAl₂O₄ as the product components after the reaction but no AlF₃. Therefore, the peak H corresponds to the sublimation endotherm of AlF₃, which is consistent with the phenomenon observed in the PTFE/Al sample.

| Temperature Range | Energy Release (J/g) |
|-------------------|----------------------|
|                   | PTFE/Al | PTFE/MnO₂ | Al/MnO₂ | PTFE/Al/MnO₂ |
| 500–650 °C        | 20.32   | 43.11     | 94.41   | 176.12       |
| 700–1000 °C       | \( / \) | \( / \)    | 129.06  | 209.14       |
As can be seen, the energy release in PTFE/Al and PTFE/MnO$_2$ samples was only 20.32 J/g and 43.11 J/g due to the endothermic decomposition of PTFE, while the exotherm of the aluminothermic reaction between Al and MnO$_2$ reached 94.41 J/g. The energy release value of the PTFE/Al/MnO$_2$ sample achieved as high as 176.12 J/g, and the heat release was much higher than those of the first three. The mutual reactions between every two reactants in the PTFE/Al/MnO$_2$ sample system exerted an overall promotion effect, so the energy release of PTFE/Al/MnO$_2$ sample was greatly enhanced. For the exothermic reaction between 700 °C and 1000 °C, the PTFE/Al/MnO$_2$ sample outperformed the Al/MnO$_2$ sample with a greater heat release, an earlier triggered reaction, a shortened reaction time, and a faster energy release. Therefore, PTFE/Al/MnO$_2$ exhibited heat release properties superior to those of PTFE/Al and Al/MnO$_2$.

4. Conclusions

In this study, DSC/TG-MS and XRD techniques were employed to analyze the reaction process at different temperatures for PTFE/Al/MnO$_2$ powdery fluorinated thermite. Meanwhile, the processes in PTFE/Al, PTFE/MnO$_2$, and Al/MnO$_2$ samples were also examined for comparison. The research can be concluded with the following results and findings.

1. PTFE oxidized Al into AlF$_3$ in the PTFE/Al sample but were reduced into CO$_2$ by Mn oxides (MnO$_2$ or Mn$_2$O$_3$) in the PTFE/MnO$_2$ sample. PTFE acted as both an oxidizer and a reducer in the PTFE/Al/MnO$_2$ sample.

2. The reaction process of the PTFE/Al/MnO$_2$ sample could be divided into two stages. In the first stage, PTFE and partial MnO$_2$ decomposed. C$_2$F$_4$, the decomposition product of PTFE, could oxidize Al into AlF$_3$ and get reduced into C. In addition, it would reduce Mn oxides (MnO$_2$ or Mn$_2$O$_3$) into MnF$_2$ and get oxidized into CO$_2$. In the meantime, Al reacted with MnO$_2$ to generate Mn$_3$O$_4$ and Al$_2$O$_3$. In the second stage, the constantly increasing temperature let excessive Al reduce Mn$_2$O$_3$/Mn$_3$O$_4$/MnF$_2$ into MnAl$_2$O$_4$ and Mn, with AlF$_3$ and Al$_2$O$_3$ produced simultaneously.

3. In the PTFE/Al/MnO$_2$ sample, the mutual reaction between each two components could promote the overall reaction. Compared with the other three systems, the ternary system exhibited a shorter reaction time, a faster energy release, and a better exothermic performance.

Author Contributions: X.F. and Y.L. conceived and designed the experiments; J.Z., J.H., Z.Y. and J.W. performed the experiments; Z.G., L.Y., S.W. and J.K. analyzed the data; J.Z. wrote the paper.

Funding: This research was funded by the National Natural Science Foundation of China (No. 51673213).

Acknowledgments: The financial support from the National Natural Science Foundation of China (General Program. Grant No. 51673213) is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflicts of interest.

References
1. Zhang, X.F.; Shi, A.S.; Qiao, L.; Zhang, J.; Zhang, Y.G.; Guan, Z.W. Experimental study on impact-initiated characters of multifunctional energetic structural materials. J. Appl. Phys. 2013, 113, 083508. [CrossRef]
2. Wang, Y. Application of Nanometer Materials and Nanocomposites in Thermites. Ph.D. Thesis, Nanjing University of Science and Technology, Nanjing, China, August 2008.
3. Osborne, D.T.; Pantoya, M.L. Effect of Al particle size on the thermal degradation of Al/Teflon mixtures. Combust. Sci. Technol. 2007, 179, 1467–1480. [CrossRef]
4. Kubota, N.; Serizawa, C. Combustion of magnesium/polytetrafluoroethylene. J. Propuls. Power 1987, 9, 539–545. [CrossRef]
5. Watson, K.W.; Pantoya, M.L.; Levitas, V.I. Fast reactions with nano-and micrometer aluminum: A study on oxidation versus fluorination. Combust. Flame 2008, 155, 619–634. [CrossRef]
6. Glavier, L.; Taton, G.; Ducéré, J.M.; Baijot, V.; Pinon, S.; Calais, T.; Rossi, C. Nanoenergetics as pressure generator for nontoxic impact primers: comparison of Al/Bi$_2$O$_3$, Al/CuO, Al/MoO$_3$ nanothermites and Al/PTFE. *Combust. Flame* **2015**, *162*, 1813–1820. [CrossRef]

7. Ye, W.J.; Wang, T.; Yu, Y.H. Research Progress of Fluoropolymer-Matrix Energetic Reactive Materials. *Aerosp. Mater. Technol.* **2012**, *42*, 19–23.

8. Li, X.Y. Preparation and Reactivity of Fluoro-Nanothermite. Ph.D. Thesis, Nanjing University of Science and Technology, Nanjing, China, March 2016.

9. Puts, G.J.; Crouse, P.L. The influence of inorganic materials on the pyrolysis of polytetrafluoroethylene. Part 1: The sulfates and fluorides of Al, Zn, Cu, Ni, Co, Fe and Mn. *J. Fluor. Chem.* **2014**, *168*, 260–267. [CrossRef]

10. Л.П. Орленко. *Explosion Physics*; Science Press: Beijing, China, 2011.

11. Osborne, D.T. The Effects of Fuel Particle Size on the Reaction of Al/Teflon Mixtures. Ph.D. Thesis, Texas Tech University, Lubbock, TX, USA, May 2006.

12. Cudzilo, S.; Szala, M.; Huczko, A.; Bystrejewski, M. Combustion reactions of poly(carbon monofluoride), (CF)$_n$, with different reductants and characterization of the products. *Propellants Explos. Pyrotech.* **2007**, *32*, 149–154. [CrossRef]

13. Zhou, X. Highly exothermic and superhydrophobic Mg/fluorocarbon core/shell nanoenergetic arrays. *ACS Appl. Mater. Interfaces* **2014**, *6*, 10497–10505. [CrossRef] [PubMed]

14. Mccollum, J.; Pantoya, M.L.; Iacono, S.T. Activating Aluminum Reactivity with Fluoropolymer Coatings for Improved Energetic Composite Combustion. *ACS Appl. Mater. Interfaces* **2015**, *7*, 18742. [CrossRef] [PubMed]

15. Lide, D.R. CRC Handbook of Chemistry and Physics 1999-2000: A Ready-Reference Book of Chemical and Physical Data. CRC *Handb. Chem. Phys.* **1999**, *15*, 504.

16. Chernenko, E.V.; Afanas’Eva, L.F.; Lebedeva, V.A.; Rozenband, V.I. Inflammability of mixtures of metal oxides with aluminum. *Combust. Explos. Shock Waves* **1988**, *24*, 639–646. [CrossRef]

17. Terayama, K.; Ikeda, M. Study on Thermal Decomposition of MnO$_2$ and Mn$_2$O$_3$ by Thermal Analysis. *Mater. Trans. JIM* **1983**, *24*, 754–758. [CrossRef]

18. Hu, X.L. Study on the preparation and kinetics of Mn$_3$O$_4$ from the deco potion of MnO$_2$. Ph.D. Thesis, Guangxi University, Nanning, China, May 2007.

19. Schoenitz, M.; Umbrjajkar, S.M.; Dreizin, E.L. Kinetic Analysis of Thermite Reactions in Al-MoO$_3$ Nanocomposites. *J. Propuls. Power* **2012**, *23*, 683–687. [CrossRef]

© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).