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Thermoanalytical investigation on pyrotechnic mixtures containing Mg-Al alloy powder and barium nitrate

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Abstract

The thermal kinetics properties of pyrotechnic compositions consist of Ba(NO₃)₂+MgAl, Ba(NO₃)₂+MgAl+S, Ba(NO₃)₂+MgAl+KClO₄ mixtures were investigated in this paper. Differential scanning calorimeter (DSC) had been employed to illustrate the reaction process of these pyrotechnic compositions. The apparent activation energy (E), frequency factor (A) and the critical ignition temperature of thermal explosion were calculated by Kissinger approach, Ozawa approach and Šatava-Šetsák approach. The results show that adding of S and KClO₄ both increase the value of E and A slightly. The critical ignition temperature of thermal explosion rises by adding of S or some KClO₄. But with the increasing of KClO₄ content, the critical ignition temperature of thermal explosion drops. Besides, the mixture consist of Ba(NO₃)₂+MgAl+S is considered unlikely to propagate detonation or deflagration, and the possibility of detonation or deflagration propagation is reduced to a certain degree when adding of KClO₄ in Ba(NO₃)₂+MgAl mixture.

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Keywords: pyrotechnic compositions; DSC; kinetic parameters; critical ignition temperature of thermal explosion; detonation propagation

Nomenclature

O.B. oxygen balance
Te onset temperature of decomposition(°C)
Tₚ peak temperature (°C)
Tₘ critical temperature of thermal explosion
Q normalized heat release (J·g⁻¹)
r² linear correlation coefficient
E activation energy (kJ·mol⁻¹)
A frequency factor(s⁻¹)

Greek symbols
β heating rate (°C·min⁻¹)

1. Introduction

The pyrotechnic compositions have a wide range of applications utilizing the production of light, heat, sound or smoke, and the pyrolants are metal-based pyrotechnic compositions containing virtually any oxidizer. In spite of the important and less-frivolous applications in civilian and military systems, the most common uses for pyrotechnic compositions are fireworks and crackers[1]. However, frequent accidents were reported in fireworks industries during processing, storage and
transportation in China and India[2]. Statistically, more than 90% of the accidents in the crackers industries associated with potassium chlorate which has a low melting point (365℃), a low decomposing temperature (400℃) and the mixtures with either sulphur or metal powder have high mechanical sensitivities[3]. Therefore, it is prohibited to use potassium chlorate in crackers and the concept of composite oxidizing agent has been proposed recently.

Except for potassium chlorate, barium nitrate is frequently used as oxidizing agent which provides a green flame and has a higher stability. Mg-Al alloy powder is an important reducing agent which used for illuminant and giving off white light. In this paper, the thermal behavior of the pyroants consist of Ba(NO_3)_2+MgAl, Ba(NO_3)_2+MgAl+S, Ba(NO_3)_2+MgAl+KClO_4 mixtures were measured by DSC. And it is followed by the thermal decomposition kinetics of the pyrotechnic compositions using multiple heating rate kinetic method. The critical ignition temperatures of these pyroants were calculated and the possibilities to propagate detonation or deflagration of these mixtures were also investigated.

2. Experiment

DSC is a routine tool for the study on the thermal stability, heat generation owing to phase transition and chemical reaction, kinetic parameters, decomposition of reactive substances and etc[4]. In this paper, the DSC apparatus used was made by Mettler Toledo (type: DSC1). A small amount of sample (about 2mg) was placed into a stainless steel crucible and heated at a constant rate (2, 5, 10, 20℃·min^{-1}) in the range from 25-500℃. The data derived from DSC experiments in nitrogen atmosphere.

Four kinds of samples were tested in this study. The proportions of the components are listed in Table 1. All the raw materials were provided by fireworks makers, dried and sieved (100 mesh) before mixed together with the ratios in practical process (do not include binders).

| Markers | Sample Contents(mass proportion) | O.B.  |
|---------|---------------------------------|-------|
| 1#      | Ba(NO_3)_2: MgAl=40:20          | -0.06 |
| 2#      | Ba(NO_3)_2: MgAl: S=40:20:25    | -0.33 |
| 3A#     | Ba(NO_3)_2: MgAl: KClO_4=40:25:20 | 0.04  |
| 3B#     | Ba(NO_3)_2: MgAl: KClO_4=30:25:30 | 0.02  |

3. Results and discussion

3.1. Thermal properties of pure compounds

The melting points and the decomposition peak temperatures of pure compounds are collected and shown in Table 2. Usually the oxidizers account for 50-70% of pyrotechnic compositions and their performances affect the sensitivity of the mixtures. According to the data, the endothermic decomposition of Ba(NO_3)_2 has a high decomposition temperatures at 621℃[5] (exceeding the measurement range of the DSC used). The first endothermic peak of KClO_4 is the phase transition peak, which is close to 308℃. The melting point of KClO_4 is observed to start at about 610℃[6-7]. The decomposition is rapidly accomplished following the melting at higher temperature with an exothermic process (also somebody thinks the first endothermic peak of KClO_4 is a sign of decomposition, which gives out a small amount of oxygen and KClO_3 is formed at the same time[5]).

| Component | Literature values[5-7] | Experimental results |
|-----------|------------------------|---------------------|
|           | Melting point/℃        | Decomposition peak temperature/℃ | Peak temperature/℃ |
| KClO_4    | 610                    | 312(-)/617(-)/627 (+) | 305(-)              |
| Ba(NO_3)_2| 592                    | 621(-)               | /                   |
| S         | 120                    | /                    | 103(-)/112(-)       |
| MgAl      | 460                    | /                    | 456(-)              |
Note: (-) means the endothermic peak, (+) means the exothermic peak, and the experimental results were obtained at the heating rate of 10°C·min⁻¹.

In addition, the melting points of the reducing agents have a certain influence on the stability of pyrotechnic compositions. For example, the Mg-Al alloy powder has a melting point of 460°C, which is much lower than the melting points of Mg and Al (both of them melt at about 650°C). And pyrotechnic mixtures with Mg-Al alloy powder as reducing agent have higher ignition temperature than the mixtures with either Mg or Al powder[3].

3.2. Thermal properties of mixtures

The DSC curves of the four kinds of pyrolants at four different heating rates are shown in Fig.1 (a-d), and the data of decomposition temperatures are shown in Table 3 also with the quantities of the heat release.

![DSC curves](image)

Fig. 1. DSC curves of (a) Ba(NO₃)₂+MgAl, (b) Ba(NO₃)₂+MgAl+S, (c) Ba(NO₃)₂+MgAl+KClO₄(O.B.=0.04) and (d) Ba(NO₃)₂+MgAl+KClO₄(O.B.=0.02) at 4 different heating rates.

It can be seen from the Fig.1 that the decomposition temperatures for the mixtures are lower than individual pure components. This phenomenon may refer to the mechanism of solid state reaction and migration of more reactive components (fuel) through the product layer to the oxidation interface. The curves show that as the heating rate increases, the decomposition peaks of mixtures shift to higher temperature and all the second peaks can’t be observed. On the other hand as shown in Fig.1 and Table 3, the initial decomposing temperatures of 2# shift to the high temperature about 10-30°C compared with 1#, which may be due to the adding of sulfur. Furthermore, the addition of sulfur changes the peak shape of the pyrolant containing Ba(NO₃)₂+MgAl, reduces the number of peaks to one. The normalized heat release of pyrolant 2#
are decreased could be caused by the reduction in oxygen content. When KClO₄ is added in sample 1# as another oxidant, the DSC curves has no significant changes except for the appearance of phase transition peak belong to KClO₄.

Table 3. Data of exothermic peak of DSC curves

| Sample | $\beta$ (°C·min⁻¹) | $T_{p1}$/°C | $T_{p2}$/°C | $Q$/J·g⁻¹ |
|--------|---------------------|------------|------------|-----------|
| 1#     | 2                   | 358.41     | 367.28     | 418.49    | 3925.57   |
|        | 5                   | 379.90     | 396.78     | 434.49    | 3048.88   |
|        | 10                  | 390.89     | 420.01     | 459.34    | 3328.67   |
|        | 20                  | 405.56     | 449.65     | /         | 2204.38   |
|        | 2                   | 373.79     | 383.69     | /         | 3482.07   |
|        | 5                   | 391.36     | 403.55     | /         | 2407.71   |
| 2#     | 10                  | 429.91     | 429.41     | /         | 1694.52   |
|        | 20                  | 429.06     | 451.64     | /         | 1466.67   |
| 3A#    | 2                   | 359.29     | 370.05     | 398.82    | 3449.40   |
|        | 5                   | 371.41     | 392.51     | 414.94    | 3129.23   |
|        | 10                  | 387.36     | 418.74     | 430.04    | 3877.87   |
|        | 20                  | 401.29     | 435.03     | 459.93    | 3469.82   |
| 3B#    | 2                   | 359.47     | 369.84     | 393.84    | 3772.06   |
|        | 5                   | 378.32     | 440.31     | 418.14    | 3905.68   |
|        | 10                  | 394.86     | 420.50     | 435.98    | 2888.07   |
|        | 20                  | 398.12     | 435.91     | 447.89    | 2654.47   |

Note: the subscripts 1 and 2 are for the first peak and the second peak respectively.

3.3. Thermal decomposition kinetics

Potential hazards associated with the thermal behavior of energetic materials require that stability evaluation and decomposition kinetics be carried out to assure their safe processing, handling and storage. In this paper kinetic parameters were determined using Kissinger approach[8], Ozawa approach[9] in the meantime and the results are shown in Table 4. The kinetic parameters showed in Table 5 were calculated by Šatava-Šetsák’s method[10], and the corresponding mechanism functions were screened out by the following expression. Among them, the subscripts s, o, k denote Šatava-Šetsák’s method, Ozawa’s method and Kissinger’s method respectively. In this case, the DSC curves obtained at heating rate of 10 °C/min were used to analyze.

$$ 0 \leq E_r \leq 400 \text{kJ/mol} \quad (1) $$

$$ \left| \frac{(E_r - E_s) / E_s} \right| \leq 0.1 \quad (2) $$

$$ \left| \frac{\lg A_s - \lg A_k}{\lg A_k} \right| \leq 0.2 \quad (3) $$

It can be seen from the Table 4 that $E_r$ calculated by Kissinger’s method is in rough agreement with that by Ozawa’s method. In addition, the pyrolant 1# consist of Ba (NO₃)₂+MgAl has the lowest activation energy in the four kinds of pyrolants and the mixture, 2# consist of Ba (NO₃)₂+MgAl+S has the highest activation energy calculated by all methods. Sample 3A# and 3B# both consist of Ba (NO₃)₂+MgAl+KClO₄, and there is a negligible difference between 3A# and 3B#’s kinetic parameters. The most probable mechanism functions of them are exactly the same, which means they have the same reaction mechanism and it can be taken as a rational result. The integral form of reaction mechanism function of 1# is Avrami-Erofeev’s equation, which means the reaction went on as random nucleation growth. The 2#’s reaction is in according with the shrinking cylinder mechanism with surface reaction rate controlling. The reaction of 3A# and 3B# controlled by the three dimensional diffusion model and the Jander equation is the most probable kinetic function.
Table 4. Kinetic parameters of thermal decomposition for pyrotechnic mixtures using Kissinger and Ozawa approach

| Sample | Kissinger | Ozawa |
|--------|-----------|-------|
|        | $E/(kJ\cdot mol^{-1})$ | $lgA/s^{-1}$ | $r^2$ | $E/(kJ\cdot mol^{-1})$ | $r^2$ |
| 1#     | 96.96     | 6.67  | 0.9976 | 102.95 | 0.9983 |
| 2#     | 119.12    | 8.33  | 0.9839 | 124.18 | 0.9868 |
| 3A#    | 118.50    | 7.45  | 0.9855 | 123.05 | 0.9879 |
| 3B#    | 118.27    | 8.41  | 0.9769 | 123.12 | 0.9802 |

Table 5. Kinetic parameters of thermal decomposition reaction calculated by Šatava-Šetáčk’s method

| Sample | The most probable mechanism function | $E/(kJ\cdot mol^{-1})$ | $lgA/s^{-1}$ | $r^2$ |
|--------|-------------------------------------|------------------------|--------------|-------|
| 1#     | $[-\ln(1-\alpha)]^{2/3}$           | 110.82                 | 7.71         | 0.9950 |
| 2#     | $1-(1-\alpha)^{1/2}$               | 117.15                 | 7.78         | 0.9957 |
| 3A#    | $[1-(1-\alpha)^{1/2}]^{1/2}$       | 115.15                 | 7.90         | 0.9667 |
| 3B#    | $[1-(1-\alpha)^{1/3}]^{1/2}$       | 116.33                 | 7.92         | 0.9805 |

3.4. Comparison of critical ignition temperature of thermal explosion

The critical ignition temperature of thermal explosion ($T_b$) is an important parameter required to insure safe storage and process operations involving explosives, propellants, and pyrotechnics. It is defined as the lowest temperature to which a specific charge may be heated without undergoing thermal runaway[11]. $T_b$ may be calculated from inflammation theory and appropriate thermokinetic parameters namely the activation energy, frequency factor, and heat of reaction. In order to obtain the critical temperature of thermal ignition ($T_b$) for the pyrolants, Eqs. (4) and (5) were used[12].

$$T_b = \frac{E - \sqrt{E^2 - 4ERT_e^0}}{2R}$$

$$T_c = T_e^0 + b\beta_0 + c\beta_0^2 + d\beta_0^3$$

In the formulas, $b$, $c$, and $d$ are coefficients; $R$ is the gas constant; $E$ is the value of activation energy obtained by Ozawa’s method. The value ($T_e^0$) of the onset temperature ($T_e$) corresponding to $\beta \rightarrow 0$ and the value of the critical temperature of thermal explosion ($T_b$) are shown in Table 6.

Table 6. Calculate results of the critical temperature of thermal explosion

| Sample | $T_e^0/\degree C$ | $T_b/\degree C$ |
|--------|-------------------|-----------------|
| 1#     | 338.15            | 347.93          |
| 2#     | 368.73            | 378.31          |
| 3A#    | 352.06            | 360.86          |
| 3B#    | 338.55            | 346.67          |

It can be seen from Table 6, among the samples, 2# has the highest $T_b$ (378.31°C) which coincides with the value of kinetic parameter. This phenomenon may be due to the reduction of oxygen balance caused by the adding of sulphur, the vaporization of sulphur absorbs heat, and it will obstruct the reaction. Moreover, from the data in Table 4 and Table 5, 3A# and 3B# have the same mechanism function and similar reaction activity, but there is more KClO₄ in sample 3B#, which provides more heat in decomposition, and it makes the $T_b$ of 3B# lower than that of 3A#. But overall, the adding of KClO₄ in the mixture of Ba (NO₃)₂+MgAl increased the value of activation energy and frequency factor, and the critical ignition temperature also increased when the content of KClO₄ was not too much.
Therefore, the complex usage of Ba (NO₃)₂ and KClO₄ was not only improve the percentage of oxygen, but also had no bad effect on the thermal stability of pyrotechnic mixtures. Moreover, using both Ba(NO₃)₂ and KClO₄ is lower-cost than applying KClO₄ as oxidant alone [3].

3.5. Comparison of the propagation probability to detonation or deflagration of pyrolants

The possibilities of detonation or deflagration propagation of pyrotechnic mixtures were estimate based on the following standard [13]: 70% 2, 4-DNT and 80% BPO (diluted with inert material, water or Al₂O₃) were used as certified reference samples. When the tested sample mixtures initiated powerfully, those who have higher sensitivity than 70% 2, 4-DNT or 80% BPO will be detonated or deflagrated, and the other will not. The $Q$ (cal) and $T_e$ (°C) of the two reference samples were tested by the same DSC, and the \( \lg Q \) vs. \( \lg (T_e-25) \) were obtained. Then the line passing through the two points of reference samples is the border line. Only when the tested sample’s point located in the upper part of the line, the detonation or deflagration might occur. The Fig. 2 shows the border line and the points of 1#, 2#, 3A# and 3B#, the data at heat rate of 10°C were used. It can be found that the sample 2# has no ability to propagate detonation or deflagration. Other samples’ probabilities of detonation are arranged as: 1#>3A#>3B#.

4. Conclusions

(1) The thermal behaviors of pyrotechnic mixtures (Ba(NO₃)₂+MgAl, Ba(NO₃)₂+MgAl+S, Ba(NO₃)₂+MgAl+KClO₄) were studied using DSC. The results show that the adding of S in mixture of Ba(NO₃)₂+MgAl shifted the initial decomposing temperature to high temperature, the activation energy, frequency factor and the critical ignition temperature of thermal explosion increased at the same time. In addition, pyrolant consist of Ba(NO₃)₂+MgAl+S mixture seems have no ability to propagate detonation or deflagration.

(2) Inclusion of KClO₄ in the mixture of Ba(NO₃)₂+MgAl also results in higher activation energy, higher frequency factor and higher critical ignition temperature of thermal explosion. But the initial decomposing temperature did not change much. With the increasing of KClO₄ content, the critical ignition temperature of thermal explosion dropped. Besides, the possibility of detonation or deflagration propagation was reduced to a certain degree when adding of KClO₄.

(3) The complex usage of Ba (NO₃)₂ and KClO₄ was conducive to saving cost and beneficial to improve the percentage of oxygen, and the pyrotechnic compositions containing these two oxidizers had a satisfactory thermal stabilities.
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