Thermal self-ignition simulation of pyrotechnic composite in different conditions

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Abstract

The combustion and explosion accidents of pyrotechnic composite occur frequently. The study on the thermal hazard of large size of pyrotechnic composite by experiment method is dangerous. It would consume huge manpower and material resources. In this paper, a study was conducted to investigate the thermal hazards of pyrotechnic composite under different ambient temperature, size and packing condition by numerical simulation method. The results show that the thermal hazards of pyrotechnic composite increase with the increase in ambient temperature. The ignition temperature of pyrotechnic composite as the inherent property of pyrotechnic composite is not affected by packing condition and size. In the same conditions, the lower thermal conductivity of packing material is, the lower SADT of pyrotechnic composite is. With the increase in the size of the grain, its SADT decreases and ignition delay period shortens, and the ignition position shifts from the center to the top of the grain with lower thermal conductivity of packing material.

Keywords Pyrotechnic composite · Thermal hazard · Packing · Size · Ambient temperature

List of symbols

A	Pre-exponential factor (s^{-1})
E	Activation energy (kJ mol^{-1})
Q	Reaction heat (kJ kg^{-1})
R	Gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
T	Temperature (K)
T_a	Ambient temperature (K)
$f(\alpha)$	Reaction mechanism function
$f(x, y, z, t)$	Known temperature function
$g(\alpha)$	Integral form of the reaction mechanism function
$g(x, y, z, t)$	Heat flux function
α	Degree of conversion (g)
c	Specific heat ($\text{J kg}^{-1} \text{K}^{-1}$)
n	Reaction order
ρ	Density (kg m^{-3})
λ	Thermal conductivity coefficient ($\text{W m}^{-1} \text{K}^{-1}$)
χ	Coefficient of heat transfer ($\text{W m}^{-2} \text{K}^{-1}$)

q'''	Heat source (W m^{-3})
Γ	Boundary of object

Introduction

In recent years, although the safety production situation of chemical industry has showed a certain improvement, the overall situation is still serious. Especially, the combustion accident of dangerous chemical warehouse in Tianjin port caused the severe personnel casualty and property loss and was a bitter, bloody lesson. It is well known that the sensitivity of energetic materials is related to the kind of energetic materials, size, ambient condition and so on. Several researches also have done a lot of work in recent years on the thermal stability and self-ignition process of energetic materials from those aspects.

Roduit [1–4] carried out their study on the thermal stability for the energetic materials with multistage decomposition by finite element method. The thermal equilibrium state of the large samples was calculated. After that, he investigated the action process of a propellant at some temperature and analyzed the critical self-ignition temperature, critical size of tank and critical temperature of the propellant. The combustion mechanism and thermal runaway of hydroxyl ammonium nitrate (HAN) was

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studied by Liu [5]. The safe storage condition for small mass of HAN was determined by thermal explosion theory. The effects of size and natural convection on critical condition of HAN with the large size were calculated by computational fluid mechanics (CFD). Jiang et al. [6] confirmed the critical size of propellant powder at a certain temperature by simulating self-ignition process. Huang et al. [7] simulated self-accelerating decomposition temperature (SADT) of cumyl hydroperoxide (CHP) with different packing material. The results show that SADT of CHP decreased with the diameter of the tank and that it was almost unaffected by the thickness of the tank. Liu et al. [8] reported the thermal stability of fireworks. The thermal explosion model of fireworks with sphere and cylinder was built by using thermal explosion theory. Furthermore, the thermal stability of fireworks under different packing material, charge structure and charge type was simulated by advanced kinetics and technology solutions (AKTS) software. The critical temperature of pyrotechnic composite obtained by theory was excellent agreement with the numerical result. Xing [9] simulated the cook-off phenomenon of RDX (hexogen) and obtained the ignition position of RDX under different ambient temperature. Dong et al. [10] studied the deflagration to detonation transition in granular HMX (octogen) explosives under thermal ignition, and he introduced the conductive burning into the classical model during simulation. The result shows that the time to detonation increases with the decrease in particle diameter. Xu et al. [11] investigated the thermal stability of ammonium nitrate in high-temperature coal seam. They found that with temperature elevated, the organic materials were oxidized by HNO_3 , which caused exothermic and gave rise to premature and misfire in blasting process. The effects of magnesium additive on the thermal behavior of Al/CuO thermites were verified by Sheikhpour et al. [12]. Addition of the magnesium powder did not initiate the reaction between micron-Al and nano-CuO, but this additive had a significant effect on the heat of reaction of nano-Al/nano-CuO system. Hoyani et al. [13] study finds that the thermal stability of HAN will be influenced during mixing metal ions like barium and calcium ions.

Pyrotechnic composite is dangerous and is easier to be ignited than other energetic materials by stimulation of energy during storage. How to reduce the accident probability and to improve the safety of pyrotechnic composite is one of the hot issues in the pyrotechnic composite research. The study on the self-ignition process of pyrotechnic composite is an important way to study its safety. Red pyrotechnic composite is a common stainer used in fireworks and tracer composite, in which safety would be affected by the safety of red pyrotechnic composite. In this paper, the safety of red pyrotechnic composite would be

first studied, and the numerical simulation method will be used.

Self-ignition process simulation

Simulation conditions

In previous DSC experiment [14], ignition temperature of the red pyrotechnic composite is 734 K, E is 192 kJ mol^{-1} , A is $2.1 \times 10^{10} \text{ s}^{-1}$. Because the pyrotechnic composite would be immediately ignited when the ambient temperature exceeding the ignition temperature of pyrotechnic composite, the self-ignition process of the red pyrotechnic composite was simulated by ANSYS at the ambient temperature of 700 K unchanged. The initial temperature of the system is assumed to be 293 K. The red pyrotechnic composite grain is stored in a contain size of A1 (height is 160 mm, the diameter is 80 mm), and the physical model of the grain is shown in Fig. 1a.

Furthermore, ambient temperature, packing condition, size and heating rate also affect the safety of pyrotechnic

Fig. 1 Physical model of the grain. **a** No packing, **b** with packing

composite during its storage and transportation. Thus, in this paper, the self-ignition process of the red pyrotechnic composite was simulated from the following four parts.

1. Effect of ambient temperature

The self-ignition processes of red pyrotechnic composite under ambient temperature of 650 and 680 K were simulated.

2. Effect of packing condition

The red pyrotechnic composition is more used to make fireworks in civil affairs, and the fireworks are generally packed by the lower thermal conductivity materials. Thus, the self-ignition process of red pyrotechnic composite packed by materials with lower thermal conductivity is simulated. Furthermore, for comparing the effect of different packing condition on red pyrotechnic composite, the self-ignition processes of red pyrotechnic composite packed by materials with higher thermal conductivity is simulated. The physical model of the grain with packing is shown in Fig. 1b. The thickness packing material is 3 mm. The ambient temperature is 700 K.

3. Effect of size

The self-ignition process of red pyrotechnic composite is simulated under the sizes including A2 (height is 120 mm, the diameter is 60 mm) and A3 (height is 200 mm, the diameter is 100 mm). The ambient temperature is 700 K.

4. Effect of heating rate

In case of fire, the ambient temperature changes with heating rate. To study the effect of heating rates on the self-ignition process of pyrotechnic composites, different magnitudes of heating rates are selected. The initial ambient temperature is 293 K. The self-ignition processes of the grain with lower thermal conductivity packing at heating rate 0.3 and 5 K min⁻¹ are simulated, respectively.

The ignition time and ignition delay period of the grain under different condition were determined. Ignition delay period is the time that the system temperature rises from ambient temperature to the ignition temperature. Ignition time includes two parts: ignition delay time and the time for the system temperature of material rises from the initial temperature to ambient temperature. The lowest ambient temperature of storage for energetic materials is an important parameter to evaluate safety of the energetic materials. According to the definition of SADT [15], SADT of energetic materials is approximately equal to its lowest ambient temperature of safety storage. Then, SADT of the red pyrotechnic composite under different condition also was calculated. The calculation time of numerical simulation is from 0 to 604,800 s.

Theoretical description

The thermal process of pyrotechnic composite is a transient process. Energy conservation equation for pyrotechnic composite can be described as Eq. (1). The heat source q''' can be expressed by Eq. (2), $f(\alpha) = (1 - \alpha)^{n-1}$.

$$\rho c \frac{\partial T}{\partial t} = \lambda \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + q''' \quad (1)$$

$$q''' = \rho^n Q A f(\alpha) \exp(-E/RT) \quad (2)$$

A lot of studies suggest that pyrotechnic composite is rarely consumed before thermal explosion happens. Therefore, the reaction of pyrotechnic composite can be as zero-order reaction. $f(\alpha)$ in Eq. (2) is 1. q''' can be simplified as Eq. (3).

$$q''' = \rho Q A \exp(-E/RT) \quad (3)$$

The material parameters used in this study are referred from the literature [16–18] and listed in Table 1.

Transient thermal analysis of ANSYS is used in the simulation. Four main parts for the simulation of ANSYS are as follows:

1. Modeling and meshing the grain.
2. Configuration physical properties of red pyrotechnic composition, packing material and the initial temperature of the system.
3. Loading boundary conditions.
4. Reaction thermokinetics.

There are three kinds of boundary conditions as follows [19].

The first-type boundary condition is determined by Eq. (4). It is applied to that the temperature of the object boundaries is known.

$$T|_{\Gamma} = f(x, y, z, t) \quad (4)$$

The second-type boundary condition is determined by Eq. (5). It is applied to that the temperature gradient of the object boundaries is known.

$$k \frac{\partial T}{\partial n} |_{\Gamma} = g(x, y, z, t) \quad (5)$$

The third-type boundary condition is that a linear combination of the temperature gradient and temperature at the boundary of the fluid medium in contact with the object. The third-type boundary condition can be expressed by Eq. (6).

$$k \frac{\partial T}{\partial n} |_{\Gamma} = \chi(T - T_a) |_{\Gamma} \quad (6)$$

Assuming the grain is set on the ground and directly exposed to the air. Then, there is a heat exchange between the top surface of the grain, the side of the grain and the air

Table 1 Parameters of materials

Material	$\rho/\text{kg m}^{-3}$	$c/\text{J kg}^{-1} \text{K}^{-1}$	$\lambda/\text{W m}^{-1} \text{K}^{-1}$	$Q/\text{kJ kg}^{-1}$
Red pyrotechnic composite	1348	1423	0.19	2722
Low thermal conductivity packing materials	550	2301	0.0357	–
High thermal conductivity packing materials	8030	502	16.27	–

when heated. The boundary condition for the top surface and the side of the grain can be dealt with the third-type boundary condition. The heat transfer coefficient is about $5 \text{ W m}^{-2} \text{ K}^{-1}$. The boundary condition for the bottom of the grain can be dealt with the first-type boundary condition.

Results and discussion

The curve of temperature versus time of pyrotechnic composite with no packing at 700 K is shown in Fig. 2. It shows that the calculated ignition temperature is 731 K, which is in good agreement with DSC experimental result (734 K) [10].

The temperature distributions of X – Y plane for the grain with no packing at different times are shown in Fig. 3. It can be seen that the high-temperature area is at the top corner of the grain when the top and the side of the grain is heated at the same time, and the temperature of the grain at the center is lower than that at the top and the side of the grain. At $3 \times 10^5 \text{ s}$, the high-temperature area is at the top surface of the grain, and the transferring form of heat is heat conduction. At $3.28 \times 10^5 \text{ s}$, there is a circular high-temperature area in the grain. It shows that the heat is mainly generated from decomposition reaction of pyrotechnic composite. With the continued heat

accumulation, the pyrotechnic composite is ignited at $3.31939 \times 10^5 \text{ s}$.

1. Ambient temperature effect

The temperature distributions at ignition of the grain with no packing under different ambient temperature are shown in Figs. 3–5. At the higher temperature, the pyrotechnic composite near the top surface of the grain is easily ignited. This is because that the heat is firstly accumulated near the top surface of the grain when the grain is heated from the top surface and the side. The ignition position of the grain with no packing would move from the top to the center of the grain as the ambient temperature decreases.

Under the different ambient temperature, the ignition time, ignition delay period, ignition temperature and ignition position of the grain with no packing are calculated and summarized in Table 2. According to Table 2, the ignition temperature of pyrotechnic composite is almost not affected by ambient temperature. The higher the ambient temperature is, the shorter the ignition time and ignition delay period become.

Figure 6 discloses the change of the grain temperature with time for no packing under different ambient temperature. The grain with no packing would be ignited once the ambient temperature is above 650 K. When ambient temperature is lower than 645 K, the grain with no packing wouldn't be ignited. So SADT of the grain with no packing is determined to be between 645 and 650 K, the average is 647 K.

2. Packing condition effect

The self-heating ignition process of the grain with packing is also simulated. The grain packed by high thermal conductivity material will input or output more heat than that packed by low thermal conductivity material. However, if the packing material is flammable, the result will be completely different. For example, the ignition point of paper is lower, and it can be ignited at about 180°C . To study the influence of packing condition on the self-heating ignition process and the thermal hazard of pyrotechnic composite, the nonflammable packing materials would be only considered.

Figure 7 shows the temperature distribution of X – Y plane of the grain ($\Phi 80 \times 160 \text{ mm}$) with lower thermal conductivity packing material at different time. At 5000 s, the higher temperature area is at the top corner of the grain.

Fig. 2 The curve of temperature versus time of grain with no packing ($\Phi 80 \times 160 \text{ mm}$) at 700 K

Fig. 3 Temperature distribution of X - Y plane of the grain with no packing ($\Phi 80 \times 160$ mm) at 700 K

Because the heat transfer coefficient for the grain at the top is the same as that at the side, the temperature distribution is an inverted U shape. At 1.5×10^5 s, the heat is transferred from the external to the internal of the grain. At 3.3×10^5 s, the higher temperature area is located at the top of the grain, and temperature distribution appears circular at 3.34×10^5 s. It can be inferred that the self-heating reaction of pyrotechnic composite is prominent. At 3.35347×10^5 s, the grain with lower thermal conductivity packing material is ignited. The ignition temperature is 731 K.

Figure 8 shows the temperature distribution of X - Y plane of the grain with the higher thermal conductivity packing material ($\Phi 80 \times 160$ mm) at different time. Because of the thermal conductivity of packing materials is higher, the heat acted on the top and side of the grain will quickly transfer to the bottom of the grain. Then, the circular temperature distribution formed in the grain. It causes

pyrotechnic composite near the center of the grain to decompose firstly. The grain with the higher thermal conductivity packing material is ignited at 3.37603×10^5 s, and its ignition position is nearly at the center.

The curves of temperature versus time of the grain with lower and higher thermal conductivity packing material at different ambient temperatures are shown in Figs. 9 and 10, respectively. From Figs. 9 and 10, it can be determined that SADT with the lower thermal conductivity packing material is between 650 and 654 K, the average is 652 K. SADT with the higher thermal conductivity packing material is between 655 and 658 K, the average is 656 K.

Table 3 summarized the ignition time, SADT and ignition position of the grain under different packing condition. In the condition of heated, the ignition time of the grain with the higher thermal conductivity packing material is the longest, and its SADT is higher than others. Then, the grain with the higher thermal conductivity packing material

Fig. 4 Temperature distribution at the ignition of the grain with no packing ($\Phi 80 \times 160$ mm) at 680 K

Fig. 5 Temperature distribution at the ignition of the grain with no packing ($\Phi 80 \times 160$ mm) at 650 K

Fig. 6 The curve of temperature versus time of grain with no packing ($\Phi 80 \times 160$ mm) under different ambient temperatures

has the best thermal stability when it is heated. Meanwhile, the ignition time of the grain with no packing is the shortest, because of the direct heating on it.

3. Size effect

Figures 11 and 12 display the temperature distribution at the ignition of the grain with the lower thermal conductivity packing for $\Phi 60 \times 120$ mm and $\Phi 100 \times 200$ mm. Compared to Fig. 3, it is clear that the ignition positions have obviously difference, the ignition positions move to the upper surface with increasing of the size. Table 4 shows the calculated results of SADT, ignition delay period and ignition position. From Table 4, it can be seen that the ignition positions of the grain with the lower thermal conductivity packing for different size ($\Phi 60 \times 120$ mm, $\Phi 80 \times 160$ mm and $\Phi 100 \times 200$ mm) is 14, 28 and 54 mm, respectively, to the top of center of grain. Furthermore, as the size of the grain rises, the ignition delay period is shortened. SADT decreased as the size increases because the greater the mass of pyrotechnic composite, the more heat released is. Compared with small size, there is a remarkable heat accumulation in the large-size grain with

Table 2 Simulation results of the grain with no packing under different ambient temperatures

Ambient temperature/K	Ignition time/s	Ignition delay period/s	Ignition temperature/K	Ignition position/mm
650	551,487	5532	731.4	14 above center
680	489,613	1809	730.8	28 above center
700	331,939	566	732.3	54 above center

Fig. 7 Temperature distribution of X–Y plane of the grain with lower thermal conductivity packing material at different time at 700 K ($\Phi 80 \times 160$ mm)

the lower thermal conductivity packing. So at the same condition, the bigger size of the grain would ignite firstly.

4. Heating rate effect

The ambient temperature rises with time during the different stages of fire. When ambient temperature rises at a certain heating rate, temperature distribution of the grain

at the ignition with the lower thermal conductivity packing is shown in Fig. 13. The ignition time with heating rate 0.3 and 5 K min^{-1} was 9551 and 529 s, respectively. Compared with the ignition time of the grain at the certain temperature of 700 K , it was obviously shortened. The ignition position moved upward the top corner of the grain.

Fig. 8 Temperature distribution of X - Y plane of the grain with the higher thermal conductivity packing material at different time at 700 K ($\Phi 80 \times 160$ mm)

Fig. 9 Curves of temperature versus time for grain with the lower thermal conductivity packing material ($\Phi 80 \times 160$ mm)

Fig. 10 Curves of temperature versus time for grain with the higher thermal conductivity packing material ($\Phi 80 \times 160$ mm)

Table 3 Simulation results for the grain at different packing conditions

Packing condition	Ignition time/s	Ignition temperature/K	SADT/K	Ignition position/mm
No packing	331,939	731.1	647	54 above center
Low thermal conductivity materials	335,347	731.6	652	60 above center
High thermal conductivity materials	337,603	732.3	656	18 above center

Fig. 11 Curves of temperature versus time for grain with the lower thermal conductivity packing material ($\Phi 60 \times 120$ mm) **Fig. 13** Curves of temperature versus time for grain with the lower thermal conductivity packing material ($\Phi 80 \times 160$ mm). **a** 529 s (5 K min^{-1}), **b** 9551 s (0.3 K min^{-1}) **Fig. 12** Curves of temperature versus time for grain with the lower thermal conductivity packing material ($\Phi 100 \times 200$ mm)

Conclusions

According to the results, the following conclusions would be obtained.

First, by the numerical simulation, the self-ignition processes of pyrotechnic composite is researched, the following parameters have been obtained, such as ignition delay period, ignition timing, ignition position and SADT, which could reflect the thermal hazards of pyrotechnic composite from different aspect.

Second, when the grain with the same size is heated at different ambient temperatures, the higher the ambient temperature is, the shorter ignition delay period of the grain is, and the more the ignition position closed to the top side of the grain. The ignition delay period and ignition position all verified that the thermal hazards of the grain increases as the ambient temperature rises. As the ambient

Table 4 Simulation results with the lower thermal conductivity packing and different sizes

Size	Ignition delay period/s	SADT/K	Ignition position/mm
$\Phi 60 \times 120$ mm	855	661	32 above center
$\Phi 80 \times 160$ mm	569	652	60 above center
$\Phi 100 \times 200$ mm	382	646	86 above center

temperature rises at a certain heating rate, the thermal hazards of the grain increase.

Third, according to SADT, it can be concluded that once pyrotechnic composite occurs as autothermic reaction, the thermal hazards of pyrotechnic composite packed by low thermal conductivity materials is higher than that packed by high thermal conductivity materials when pyrotechnic composite is accidentally heated. Thus, it is necessary to keep fireworks at low ambient temperature and to avoid exposing to heat during its production, storage or transportation.

Fourth, at the same ambient temperature, once self-heating reaction of the pyrotechnic composite occurs, the grain with a big size will ignite firstly. The result shows that the thermal hazards of pyrotechnic composite packed by low thermal conductivity material increases with the increase in size. Thus, fireworks should avoid extensive stores.

Moreover, the research results are also available for guiding other pyrotechnic composition or energetic materials.

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