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THE THERMAL BEHAVIOR OF POWDER EMULSION EXPLOSIVES

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Abstract

The determination of the most probable mechanism function and the calculation of kinetic parameters of thermal decomposition of powder emulsion explosives have been achieved by different kinetic equations and different kinetic methods from data non-isothermal SC-DSC curves, DSC curves, and thermal explosion delay curve. The courses which the reaction would follow under adiabatic conditions are predicted.

Keywords: DSC, non-isothermal kinetic, powder emulsion explosive, thermal decomposition, thermal explosion

Introduction

Emulsion explosives [1–3] have gained world-wide application in blasting industry in the recent twenty years, because of their surprising water-resistance, high velocity of detonation, good sensitivity at small diameters, low susceptibility to environmental temperature, and low susceptibility to accidental initiation [3]. Therefore, emulsion explosives have replaced most other types of cartridged or pumpable explosive and blasting agents in the blasting industry. However, almost all of emulsion explosives being used in commercial blasting are in the grease-like state at ambient temperature. This grease-like state causes inconveniences in production, especially in storage, transportation, and employment. Therefore, powder emulsion explosives have been devised [4–6]. They do not need any additional hollow (glass, plastic, or gas) microballons in order to increase their sensitivity to detonation at small diameters, and their variable partical sizes make them adaptable to the different blasting operations. The blast

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dust characteristics of powder emulsion explosives have been investigated [7–8].

In this paper the thermal decomposition behaviour and thermal explosion behaviour of powder emulsion explosive were studied by SC-DSC curves, DSC curves, and temperature-explosion delay curve. The most probable mechanism function and kinetic parameters of thermal decomposition of powder emulsion explosive were obtained, and the courses by which the reaction would follow adiabatically may then be predicted.

Experimental

The composition of powder emulsion explosive is shown in Table 1. The material used in our study was supplied by Beijing General Research Institute of Mining and Metallurgy [5].

Table 1 The composition of powder emulsion explosive

Components	Composition /mass %	Components	Composition /mass %
Salts nitrate	87	Composted wax	4
Urea	2	Emulsifier	2
Water	4	Active carbon	1

DSC experiments were carried out on a Perkin DSC-2 with an aluminium cell. SC-DSC experiments were carried on a Shanghai Balance Manufacture's CDR-1 Differential Scanning Calorimeter with a sealed stainless steel cell [9]. The thermal explosion delay experiments were conducted on an explosion temperature measuring device.

Kinetic analysis and calculation

For kinetic analysis and calculations, the two following equations were employed

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

and

$$G(\alpha) = kt \tag{2}$$

where t is the time (s), α is the fraction reacted, $f(\alpha)$ and $G(\alpha)$ are the differential and integral form of mechanism function, k is the kinetic constant (1/s). The relationship between $f(\alpha)$ and $G(\alpha)$ is

$$f(\alpha) = \frac{1}{G'(\alpha)} \tag{3}$$

The relationship between the kinetic constant (k) and the absolute temperature (T) of reaction is expressed by Arrhenius equation

$$k = A\mathrm{e}^{-E/RT} \tag{4}$$

where A is the pre-exponential constant (1/s), E is the activation energy (J/mol), R is the gas constant (J/mol·K).

The temperature change is represented by

$$T = T_o + \varphi t \tag{5}$$

where T is the temperature (K), T_o is the starting temperature (K), φ is the constant heating rate. Equations (1), (4) and (5) are combined to yield

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\varphi}\mathrm{e}^{-E/RT} \tag{6}$$

Different kinetic mechanisms correspond with different $f(\alpha)$ or $G(\alpha)$. Table 2 shows the most common forms of $f(\alpha)$ and $G(\alpha)$. We want to choose and identify the most probable mechanism function among the function forms in Table 2 by such methods of kinetic calculation, as the two-point method [10], Kissinger [11], Ozawa [12], differential methods (Achar [13] and Phadnis [14]), and integral methods (MacCallum [15], Satava [16], Agrawal [17], Universal [9]). We can also obtain kinetic parameters of thermal decomposition from SC-DSC curves, DSC curves and thermal explosion delay curve by the best linear regression.

Tables 3, 4 and 5 list the data of powder emulsion explosive determined by SC-DSC, DSC, and thermal explosion delay (*TED*) experiments, respectively. The regression results for thermal decomposition of the sample are given in Table 6. The most probable mechanism function for the thermal decomposition in sealed stainless steel cell is $1-(1-\alpha)^{1/3}$ (integral form) or $3\cdot(1-\alpha)^{2/3}$ (differential form). The activation energy is about 130±10 kJ/mol and A is about 9.93×10^{9}~6.61×10^{13} (1/s).

Adiabatic behavior prediction

For a reaction occurring in an adiabatic system, the enthalpy change for the system ($\mathrm{d}H_{sys}$) is zero by definition, and the heat of reaction raises the temperature of the whole system according to the following thermodynamic equation

Table 2 Mechanism functions for reaction kinetics

Name	Mechanism	$G(\alpha) = kt$	$f(\alpha) = \frac{1}{k}\cdot\frac{d\alpha}{dt}$
Power law	1D	α^2	$\frac{1}{2}\alpha^{-1}$
	2D	$\alpha + (1-\alpha)\ln(1-\alpha)$	$-\frac{1}{\ln(1-\alpha)}$
	2D,$n = \frac{1}{2},2$	$\left[1-(1-\alpha)^{\frac{1}{2}}\right]^{n}$	$\frac{3}{n}\cdot(1-\alpha)^{\frac{2}{3}}\cdot\left[1-(1-\alpha)^{\frac{1}{3}}\right]^{(1-n)}$
	3D,$n = \frac{1}{2},2$	$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^{n}$	$\frac{2}{n}\cdot(1-\alpha)^{\frac{1}{2}}\cdot\left[1-(1-\alpha)^{\frac{1}{2}}\right]^{(1-n)}$
Ginstling-Brounstein	3D	$1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}$	$\frac{3}{2}\left[(1-\alpha)^{\frac{1}{3}}-1\right]^{-1}$
	3D	$\left[(1+\alpha)^{\frac{1}{3}}-1\right]^{2}$	$\frac{3}{2}(1+\alpha)^{\frac{2}{3}}\left[(1+\alpha)^{\frac{1}{3}}-1\right]^{-1}$
Zhuralev-Lesokin-Tempelman	3D	$\left[(1-\alpha)^{-\frac{1}{3}}-1\right]^{2}$	$\frac{3}{2}(1-\alpha)^{\frac{4}{3}}\left[(1-\alpha)^{-\frac{1}{3}}-1\right]^{-1}$
Avrami-Erofeev	$n = \frac{1}{4},\frac{1}{3},\frac{2}{5},\frac{1}{2},\frac{2}{3},\frac{3}{4},1,\frac{3}{2},2,3,4$	$[-\ln(1-\alpha)]^{n}$	$\frac{1}{n}(1-\alpha)[-\ln(1-\alpha)]^{(1-n)}$
Prout-Tompkins	B1	$\ln\frac{\alpha}{1-\alpha}$	$\alpha(1-\alpha)$
Mampel Power	$n = \frac{1}{4},\frac{1}{3},\frac{1}{2},1,\frac{3}{2},2$	α^{n}	$\frac{1}{n}\alpha^{(1-n)}$
Chemical reaction	$n = \frac{1}{4},\frac{1}{3},\frac{1}{2},2,3,4$	$1-(1-\alpha)^{n}$	$\frac{1}{n}(1-\alpha)^{(1-n)}$
		$(1-\alpha)^{-1}$	$(1-\alpha)^{2}$
		$(1-\alpha)^{-1}-1$	$(1-\alpha)^{2}$
		$(1-\alpha)^{-\frac{1}{2}}$	$2(1-\alpha)^{\frac{3}{2}}$
Exponential law	$n = 1,2$	$\ln\alpha^{n}$	$\frac{1}{n}\alpha$

Table 3 Data determined by SC-DSC for differential and integral calculations

No.	T_i /K	α_i	$(\mathrm{d}H/\mathrm{d}t)_i$ /mJ·s^{-1}
1	491.2	0.0206	0.532
2	498.9	0.0263	0.860
3	502.7	0.0455	1.503
4	507.2	0.0760	1.854
5	511.2	0.0845	2.330
6	514.7	0.0979	2.654
7	518.7	0.1199	3.103
8	522.7	0.1518	3.662
9	525.7	0.1795	4.218
10	526.7	0.2185	4.777
11	530.7	0.2497	5.710
12	532.2	0.2821	6.014

φ=10.76 deg·min^{-1}, T_o=470.4 K, H_o=2383 mJ, T_g=516.7 K, α_g=0.1010

Table 4 Data for Kissinger and Ozawa methods

SC-DSC		DSC	
φ_i /deg·min^{-1}	T_{mi} /K	φ_i /deg·min^{-1}	T_{mi} /K
1.99	505.4	5.00	515.1
5.06	521.2	10.00	526.2
10.76	532.2	20.00	535.0
22.15	542.1	40.00	548.6

Table 5 Data determined by thermal explosion delay experiments

T /K	t /s	T /K	t /s
606.2	3.08	594.2	6.50
604.2	4.10	592.2	7.10
602.2	4.71	588.2	7.82
600.2	4.87	586.2	8.44
596.2	5.68		

$$\mathrm{d}H_{sys} = \mathrm{d}H_{reac} + C_p \cdot \mathrm{d}T \tag{7}$$

C_p may be considered as a constant, which is 2.4 J/g ·K and equals the value of ammonium nitrate at 120°C. Equation (7) can be integrated from T_o to T

Table 6 The regression results for the kinetic parameters

Method	Equation	$G(\alpha)$	E /kJ·mol^{-1}	lg A	r	s
SC-DSC	Two points	$1-(1-\alpha)^{1/3}$	143.0	11.72		
	Kissinger		131.4	10.88	0.9983	0.0653
	Ozawa		133.1		0.9985	0.0283
	Achar	$1-(1-\alpha)^{1/3}$	132.0	9.97	0.9907	0.0515
	Phadnis	$1-(1-\alpha)^{1/3}$	130.8		0.9974	0.0061
	MacCallum	$1-(1-\alpha)^{1/3}$	135.6	10.30	0.9909	0.0552
	Satava	$1-(1-\alpha)^{1/3}$	136.2	10.42	0.9909	0.0552
	Agrawal	$1-(1-\alpha)^{1/3}$	134.7	13.82	0.9897	0.1273
	Universal	$1-(1-\alpha)^{1/3}$	136.3	9.11	0.9900	0.1272
DSC	Kissinger		139.5	11.87	0.9968	0.0820
	Ozawa		141.0		0.9972	0.0355
TED			122.6		0.9936	0.0756

$$-\Delta H_{\mathrm{reac}} = C_{\mathrm{p}}(T - T_{\mathrm{o}}) \tag{8}$$

Because the fraction reacted α is defined as

$$\alpha = \frac{\Delta H_{\mathrm{reac}}}{\Delta H_{\mathrm{total}}} \tag{9}$$

Equations (8) and (9) are combined to give

$$\alpha = -\frac{C_{\mathrm{p}}}{\Delta H_{\mathrm{total}}}(T - T_{\mathrm{o}}) \tag{10}$$

This indicates that the fraction reacted is a simple function of temperature for an adiabatic system. In fact the relationship is linear, ranging from $\alpha=0$ at T_{o} to $\alpha=1$ at the final adiabatic temperature T_{f} given by

$$T_{\mathrm{f}} = T_{\mathrm{o}} - \frac{\Delta H_{\mathrm{total}}}{C_{\mathrm{p}}} \tag{11}$$

Then Eq. (9) is differentiated by time and rearranged to obtain

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\Delta H_{\mathrm{reac}}}{C_{\mathrm{p}}}\cdot\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{12}$$

where $\mathrm{d}T/\mathrm{d}t$ is known as the self-heating rate. The relationship between time (induction time) and the self-heating rate is

$$t = \int_{T_{\mathrm{o}}}^{T} \frac{1}{(\mathrm{d}T/\mathrm{d}t)}\,\mathrm{d}T \tag{13}$$

Table 7 The adiabatic behaviour prediction of powder emulsion explosives

Start temperature /°C	Induction time /min	Fraction reaction
80	1693	0.1013
90	5223	0.0912
100	1717	0.0811
110	600	0.0711
120	220	0.0610
130	85	0.0509
140	34	0.0408

For the powder emulsion explosive studied, $G(\alpha)$ is $1-(1-\alpha)^{1/3}$, $f(\alpha)$ is $3\cdot(1-\alpha)^{2/3}$, ΔH_{total} is 2383.6 J/g, A is 7.58×10^{10} (1/s), E is 131.4 kJ/mol. By numerical integration, the starting point is at T_o, and the calculation can be stopped at any chosen value of dT/dt (e.g., 10 deg·min^{-1}). The results calculated are summarised in Table 7. Therefore, we may draw a conclusion that the processes of production of powder emulsion explosives, when carried out below 100°C, are safe only if the thermal safety is considered even if under adiabatic conditions.

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Zusammenfassung — Mittels verschiedener kinetischer Gleichungen und verschiedener kinetischer Methoden wurde anhand der Angaben aus nichtisothermen SC-DSC-Kurven, DSC-Kurven und thermischer Explosionsverzugskurven die wahrscheinlichste Mechanismusfunktion der thermischen Zersetzung von Pulveremulsions-Sprengstoffen ermittelt und die diesbezüglichen kinetischen Parameter berechnet. Der Reaktionsweg unter adiabatischen Bedingungen wird vorausgesagt.