Thermal decomposition of multiple-based nitramine propellants

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As a multiple-based propellant, nitramine's decomposition attributes to those of components, but not to their simple plus. Three typical prescriptions of multiple-based propellant, which are RNG (containing nitroguanidine, NGu), RHN (containing hexanitrostilbene, HNS) and RNO (nano-oxides added), are tested. Here Ozawa method is used to deal with the data gained from thermogravimetry (TG) and to analyze its thermal decomposition mechanism and activation energies. As a result, it is evident that nitramine decomposition mainly undergo two stages. Compared to RNG whose mechanism functions are F_1 (random nucleation) and D_3 (three-dimensional diffusion) for each stage, RHN maintains the same mechanism function, but exhibits lower activation energies. While it is rather peculiar that nano-oxides in RNO can not only lower activation energies, but also change the mechanism function which become R_2 (interface reaction) and D_1 (two-dimensional diffusion) respectively. It shows that nano-oxides has a certain effect to catalyze the thermal decomposition and combustion of nitramine significantly.

Key words: nitramine propellant, thermal decomposition, nano-oxides

1. Introduction

Consisting of multiple ingredients, nitramine's thermal decomposition is relevant to those of components, but not to their simple plus. Combustion experiments shows that HNS and nano-oxides may change burning rate of propellant[1]. However, the reaction mechanism is far beyond made clear. Usually influenced by some coordinating effect or even catalysis of a certain or more components, the thermal decomposition presents complicated multiple-stage characteristics, for example, the maxim exothermal peak on its DSC curve is an overlapping one. It's difficult to distinguish its two main specific peaks, which respectively stand for exothermals of NNC_2 and RDX[2,3]. For this reason, Ozawa method is employed to clarify the kinetic characteristics of each stage.

2. Experimental

2. 1 Samples

Three propellant's samples, whose ingredients are listed in Table 1, are selected to test. The size of Nano-oxide is 10 nm.

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2. 2 Apparatus

Thermogravimetry tests (TG) were carried out by using Shimadzu DTA-50 Analysis, varing the heating rates from 5 to 30℃/min, interval of 5℃/min. The amount of filled sample was 1 mg, surrounded by nitrogen whose fluxing rate is 20 ml/min.

3. Analysis and Discussion

3. 1 Principle of Ozawa Method

Ozawa, one of non-isothermal methods, is a dynamic one to mainly deal with TG curves under different heating rate[4]. As shown in Fig.1, on a typical TG curve c is the conversion ratio or mass fraction of remainder, defined as W/W_0, where W is the mass of remainder and W_0 is the mass of total reactant. When the propellant decomposes, the mass loss rate can be expressed by

$$-\frac{dc}{dt} = kf(c) \qquad (1)$$

where f(c) is a function of mass decomposition

Table 1 Chemical compositions of the propellants tested in this study

	NNC_2	RDX	NGu	HNS	Nano-oxide	DBP
RNG	56.5%	27.0%	15.0%			1.5%
RHN	60.0%	32.0%		5.0%		1.5%
RNO	60.5%	32.5%		5.0%	0.5%	1.5%

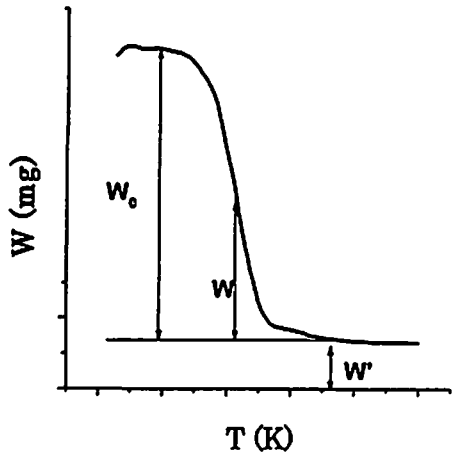

Fig. 1 Definition of analysis for TG curve

defined as "mechanism function" and k is reaction rate defined by

$$k = Ae^{-Ea/RT} \tag{2}$$

where Ea is activation energy, T is temperature, R is gas constant, and A is pre-exponential constant. Substituting Eq. (1) into Eq. (2), one gets

$$\frac{dc}{dt} = Ae^{-Ea/RT} f(c) \tag{3}$$

Substituting the heating rate Φ, which is defined as dT/dt, into Eq. (3), one gets an expression of

$$-\frac{dc}{dT} = \frac{A}{\Phi} e^{-Ea/RT} f(c) \tag{4}$$

Transforming TG curves at different heating rates to a series of curves of logarithm of heating rate by reciprocal of temperature, $\mathrm{Log}\Phi - 1/T$ curves at different remainder percentage can be plotted. If all these straight lines obtained are parallel, it can be drawn that the mechanism of sample is unchangeable during the whole thermal decomposition. Then the regressive equation is:

$$\mathrm{Log}\,\Phi = \mathrm{Log}\{AE_a/Rf(c)\} - 2.314 - 0.4567E_a/RT \tag{5}$$

From the slope of $\mathrm{Log}\Phi - 1/T$ (equal to $-0.4567E_a/R$), the activation energy can be determined. Otherwise, if the slope does not appear a straight line, the sample's thermal decomposition is not a single step reaction, and $\mathrm{Log}\Phi - 1/T$ curves appear more than one set of parallel lines, in which only parallel ones at adjacent remainder mass fractions stand for one type of mechanism. By slope of different parallel lines, Ea of each stage can also be determined.

3. 2 Nitramine's Thermal Decomposition

In the discussion, RNG is a reference sample and the other two are modified, among which RHN includes HNS substituting for NGu, whereas RNO is added by 0.5% nano-oxide. Their $\mathrm{Log}\Phi - 1/T$ curves at different remainder percentages are shown in Figs. 2 - 4. From the figures, we can see that all these curves of the three samples are divided by two groups. When c is larger, the curves present one set of parallels whose slopes are smaller, whereas c is smaller, the curves present another set of parallels

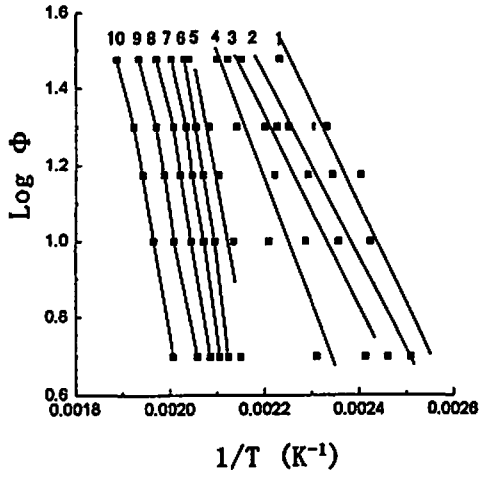

Fig. 2 Log Φ - 1/T curves of RNG

(Note: numbers 1 to 10 correspond to curves under different c values, such as from 0.95 to 0.80, interval of 0.05 for the first four, and from 0.70 to 0.20, interval of 0.10 for the others)

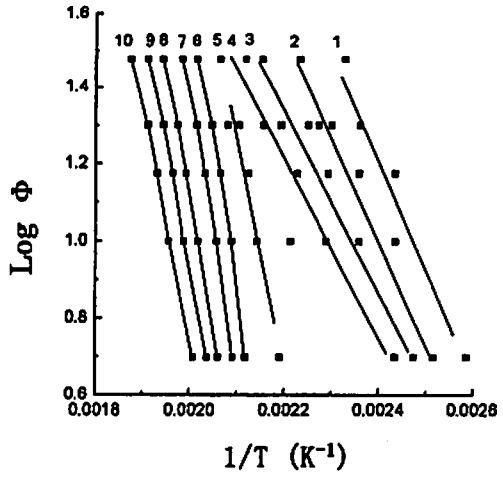

Fig. 3 Log Φ - 1/T curves of RHN

(Note: numbers 1 to 10 correspond to curves under different c values, such as from 0. 95 to 0. 80, interval of 0. 05 for the first four, and from 0. 70 to 0. 20, interval of 0. 10 for the others)

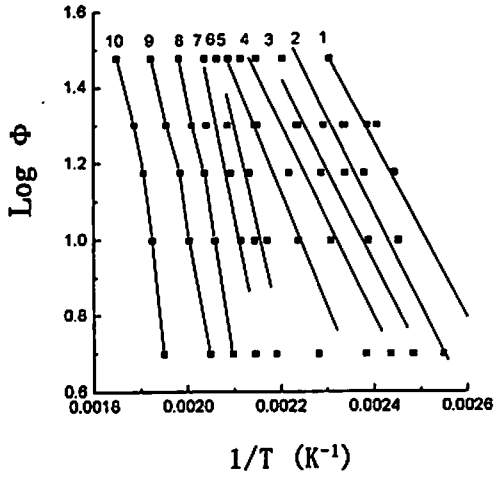

Fig. 4 Log Φ - 1/T curves of RNO

(Note: numbers 1 to 10 correspond to curves under different c values, such as from 0. 95 to 0. 80, interval of 0. 05 for the first four, and from 0. 70 to 0. 20, interval of 0. 10 for the others)

whose slopes are bigger. It suggests this suggesting that nitramine's thermal decomposition undergoes two stages. By Eq. (5), one can calculate the activation energies for each stage, as listed in Table 2, which shows that the values of E_a for the three samples come into a decreasing sequence by RNG, RHN and RNO.

3. 3 Mechanism Function

The mechanism function is given by Ozawa as

$$\ln (AE_a/R\Phi) = \ln f(c) - \ln P(Y) \qquad (6)$$

Table 2 Activation energies of the propellants tested

	C (%)	E_a (KJ/mol)
RNG	95～75	49. 10
	75～10	134. 64
RHN	95～75	47. 70
	75～10	121. 58
RNO	95～75	44. 34
	75～10	97. 18

where $\ln (AE_a/R\Phi)$ is a constant irrelevant to temperature for a certain Φ, whereas ln P(Y) is a linear function of 1/T for a proper reaction mechanism, so ln f(c) is also bound to be a linear function of 1/T. There are 30 types of the f(c) forms, the common nine and their corresponding reaction mechanism among them being listed in Table 3.

Selecting Φ by 10℃/min, ln f(c)-1/T curves of each function for RNG, RHN and RNO are plotted in Figs. 5 - 7, and meanwhile ln P(Y)-1/T curves are obtained by the following equation:

$$ln\,P(Y) = -1.052\,E_a/RT \qquad (7)$$

That is, if ln f(c)-1/T is parallel to ln P(Y)-1/T, then this f(c) is just the thermal reaction mechanism function for the sample. In Figs. 5 - 7, ln f(c)-1/T curves for the three samples are all made up of two segments of lines, corresponding to their two thermal decomposition stages respectively, indicting that these f(c)s stand for their thermal reaction mechanism function. From the result shown in Table 4, it can be concluded that RNG and RHN have the same mechanism functions for both stages, while RNO is quite different from them.

4. Results

Nitramine's thermal decomposition undergoes two stages, and for each stage E_a and F(c) are different. These two stages are mainly caused by the thermal decomposition of binder (NNC_2) and oxidizes (RDX, NGu, or HNS). After HNS substituting for NGu, mechanism of RHN's thermal decomposition is unchangeable, only E_a value of each stage is smaller than that of RNG.

Having been added by nano-oxydize, not only E_a

Table 3 Common types of the f(c)

Type of reaction mechanism function	Procedure controlling reaction rate
$D_1 = (1-c)^2$	one-dimensional diffusion
$D_2 = c\ln c + (1-c)$	two-dimensional diffusion, cylindrical symmetry
$D_3 = (1-c^{1/3})^2$	three-dimensional diffusion, spherical symmetry Jander equation
$D_4 = (1+2c)/3 - c^{2/3}$	three-dimensional diffusion, spherical symmetry Ginstling-Browns Stein equation
$F_1 = -\ln c$	random nucleation, one nuclear for a particular
$A_2 = (-\ln c)^{1/2}$	random nucleation, Avrami equation I
$A_3 = (-\ln c)^{1/3}$	random nucleation, Avrami equation II
$R_2 = 1-c^{1/2}$	interface reaction, cylindrical symmetry
$R_3 = 1-c^{1/3}$	interface reaction, spherical symmetry

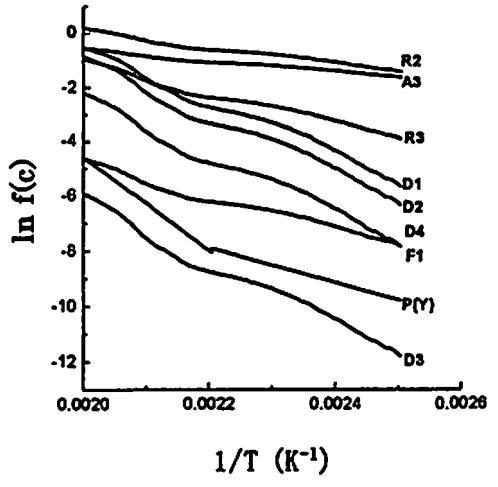

Fig. 5 Mechanism function of RNG

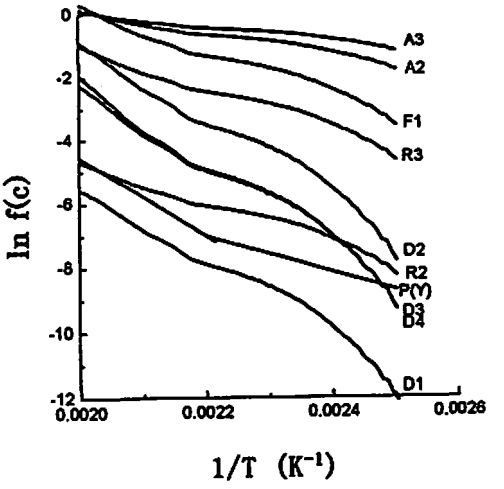

Fig. 7 Mechanism function of RNO

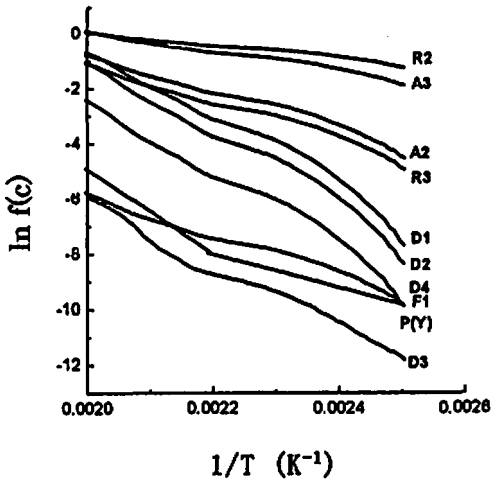

Fig. 6 Mechanism function of RHN

Table 4 Reaction mechanism function for the propellants tested

	C (%)	Function f(c)
RNG	95～75	F_1
	75～10	D_3
RHN	95～75	F_1
	75～10	D_3
RNO	95～75	R_2
	75～10	D_1

value but also thermal decomposition functions of RNO are different from those of RNG and RHN. Its

E_a is the smallest in the three samples, and compared to RNG and RHN, its mechanism function f(c) for each stage changes from F_1 (random nucleation) and D_3 (three-dimensional diffusion) to R_2 (interface reaction) and D_1 (two-dimensional diffusion), respectively. It shows that nano-oxides can catalyze the thermal decomposition and combustion of nitramine significantly.

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