Thermal behavior and non-isothermal decomposition reaction kinetics of catalyzed hniw-cmdb propellant

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Abstract: The thermal behavior under pressure of 0.1, 4, and 7 MPa and non-isothermal decomposition reaction kinetics under pressure of 4 and 7 MPa of the composite modified double base propellant containing hexanitrohexaazaisowurtzitane (HNIW-CMDB propellant) was investigated by differential scanning calorimetry (DSC). The results showed that there are two exothermic peaks on DSC curve under 0.1 MPa. The exothermic peak temperature decreases with surroundings pressure increasing. There is only one exothermic peak on every high pressure DSC curve. The exothermic peak temperature under every pressure increases with heating rate increasing. The exothermic decomposition kinetic parameters of the propellant changed while the reaction mechanism function didn’t change when catalyzer was added into propellant or testing surroundings changed. The kinetic equation of exothermic decomposition reaction mechanism under 4 MPa and 7 MPa are Avrami-Erofeev (n=2/3).

1. Introduction

Increasing the energy of propellants is the eternal theme of propellant development in various countries. It is an important means to add high energy density compounds to propellants. Hexanitrohexaazaisowurtzitane (HNIW) is one of the most representative compounds [1, 2]. HNIW is an ecologically safe, high-energy density material with a cage structure. It can increase the specific impulse and density of solid propellant largely. It is considered as the most powerful explosive and has great applying value in solid propellant field. In view of its superior performance, HNIW can be regarded as a deputy of the next generation propellant raw material. It can greatly improve the energy and burning rate of solid propellants, and its application to high energy solid propellants has a good effect on improving the energy performance, safety and smokeless properties of this kind of propellants.

The thermal decomposition mechanism, thermal decomposition kinetics and interaction with other energetic materials have been reported [3-7]. The research on the effect of HNIW on the energy performance, combustion performance and thermal decomposition of propellant has been carried out [8-13]. The results show that the burning rate and pressure index of the modified double base propellant containing HNIW (HNIW-CMDB) are higher than that of the modified double base propellant containing RDX or HMX. At present, the investigation on regulating the combustion performance of HNIW-CMDB...
propellants is still being on. In order to reduce the pressure index, in this work, the decomposition performance and reaction kinetics of HNIW-CMDB propellant containing lead salt catalyst have been investigated by non-isothermal method and differential scanning calorimetry technique (DSC).

2. Experimental

2.1. Sample

The based sample used in the experiments is HNIW-CMDB propellant whose composition by mass percent are 64.7% of nitrocellulose and nitroglycerin, 28% of HNIW and 7.3% of other auxiliary additives. The other samples were made by based sample added special lead salt catalyst (B-Pb). The strand samples are prepared by a solventless extrusion technique.

2.2. Equipment and conditions

The DSC experiments are carried out on a differential scanning calorimeter (Model DSC910S, TA Co., USA). Samples of less than 2.00 mg are heated at the heating rates (β) of 5, 10, 20, 25 K·min⁻¹. Pressure is obtained by filling nitrogen gas (purity, 99.999%) in the heating furnace.

3. Results and discussion

3.1. Thermal decomposition behaviors of HNIW-CMDB propellant

The DSC curves at the heating rates (β) of 10 K·min⁻¹ under different pressure for catalyzed HNIW-CMDB propellant sample are shown in Fig.1. There are two exothermic peaks on DSC curve under 0.1 MPa, while only an exothermic peak on every DSC curve under pressure, which appears very different with that under 0.1 MPa. It indicates pressure influence thermal decomposition process greatly, which is mainly concentrated in the exothermic district of the propellant sample. With the increase of pressure, the peak temperature of main exothermic decomposition of propellant shifted towards lower temperature. It is mainly attributed to the decomposition of the NC, NG and partly HNIW. The DSC curves at different heating rates under 4 MPa and 7 MPa for catalyzed HNIW-CMDB propellant sample are shown in Fig. 2. With the increase of heating rate, the onset temperature, peak temperature and final temperature of the exothermic decomposition of propellant shifted towards higher temperature. The exothermic peak temperature at same heating rate decreases with pressure increasing.

Figure 1. DSC curves for catalyzed sample at different heating rates and pressure.

![DSC curves](image-url)
3.2. The calculation of non-isothermal reaction kinetics

In order to study the thermal decomposition mechanism of the main exothermic reaction stage (main exothermic peak) under propellant working pressure, obtain the corresponding kinetic parameters [apparent activation energy (E₉), pre-exponential constant (A)] and the most probable kinetic model function, and compare the difference of these kinetic parameters between propellant working pressure and other pressure, the DSC curves at heating rates of 5, 10, 20 and 25 K·min⁻¹ were dealt by mathematic means, and five integral methods [Eqs. (1)-(5)] and one differential methods [Eq.(6)] listed in table 1 are employed [14].

Table 1. Kinetic analysis methods.

| Method                        | Equation                                                                 |
|-------------------------------|--------------------------------------------------------------------------|
| Ordinary-integral             | \[ \ln[G(\alpha)/T^{2}] = \ln[(AR/\beta E)(1 - 2RT/E)] - E/RT \] (1)     |
| Mac Callum-Tanner             | \[ \lg[G(\alpha)] = \lg(AE/\beta R) - 0.482E^{0.4557} - (0.449 + 0.217E)/(0.001T) \] (E/kcal·mol⁻¹) (2) |
| Šatava-Šesták                 | \[ \lg[G(\alpha)] = \lg(A_{k}E_{s}/\beta R) - 2.315 - 0.4567E_{s}/RT \] (3) |
| Agrawal                       | \[ \ln[G(\alpha)/T^{2}] = \ln[(AR/\beta E)(1 - 2(RT/E))(1 - S(RT/E)^{2})]/E/RT \] (4) |
| Flynn-Wall-Ozawa              | \[ \lg \beta = \lg[AE/(RG(\alpha))] - 2.315 - 0.4567E/RT \] (5)          |
| Kissinger                     | \[ \ln(\beta/T_{m}^{2}) = \ln(A_{l}R/E_{l}) - E_{l}/RT_{m}, \ i = 1,2,\ldots,4 \] (6) |

Where \( \alpha \) is the conversion degree of sample reacted; \( T \) is the temperature (K) at time \( t \); \( T_{0} \) is the temperature of the initial point at which DSC curve deviates from the baseline; \( R \) is the gas constant; \( f(\alpha) \) and \( G(\alpha) \) are the differential model function and the integral model function, respectively, and the means of \( E_{a}, \ A, \ \beta \) and \( T_{p} \) are mentioned before. The data needed for the equations of the integral and differential methods, \( i, \alpha_{i}, \beta, \ T_{i}, \ T_{a}(\text{onset temperature}), \ T_{p}, \ (da/dT)_{i}, \ i = 1,2,3,\cdots, \) are obtained from the DSC curves and summarized in table 2.

Table 2. Data for decomposition processes of catalyzed sample at different heating rates from DSC curves.

| \( \alpha \) | \( \beta / \text{K·min}^{-1} \) | \( T / \text{K under 4 MPa} \) | \( \beta / \text{K·min}^{-1} \) | \( T / \text{K under 7 MPa} \) |
|-------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
|             | 5                               | 10                             | 20                             | 25                             | 5                               | 10                             | 20                             | 25                             |
| 0.02        | 170.1                           | 177.4                          | 185.9                          | 189.2                          | 443.5                           | 449.1                          | 449.1                          | 453.6                          |
| 0.04        | 174.9                           | 182.8                          | 191.6                          | 194.6                          | 448.5                           | 454.6                          | 454.6                          | 461.6                          |
| 0.06        | 177.6                           | 186                            | 195                            | 197.9                          | 451.3                           | 457.8                          | 457.8                          | 466.4                          |
| 0.08        | 179.6                           | 188.2                          | 197.4                          | 200.4                          | 453.2                           | 460.1                          | 460.1                          | 469.5                          |
| 0.10        | 181.1                           | 190                            | 199.3                          | 202.3                          | 454.7                           | 461.8                          | 461.8                          | 471.8                          |
| 0.12        | 182.4                           | 191.5                          | 200.9                          | 203.9                          | 455.9                           | 463.2                          | 463.2                          | 473.6                          |
| 0.14        | 183.6                           | 192.8                          | 202.3                          | 205.4                          | 457                            | 464.5                          | 464.5                          | 475.2                          |
| 0.16        | 184.5                           | 194                            | 203.6                          | 206.7                          | 457.8                           | 465.6                          | 465.6                          | 476.5                          |
| 0.18        | 185.4                           | 195                            | 204.7                          | 207.8                          | 458.7                           | 466.6                          | 466.6                          | 477.7                          |
| 0.20        | 186.3                           | 196                            | 205.7                          | 208.9                          | 459.4                           | 467.5                          | 467.5                          | 478.8                          |
| 0.22        | 187.1                           | 196.8                          | 206.7                          | 209.9                          | 460                            | 468.3                          | 468.3                          | 479.8                          |
| 0.24        | 187.9                           | 197.7                          | 207.6                          | 210.8                          | 460.7                           | 469                            | 469                            | 480.7                          |
| Tp | 188.6 | 198.5 | 208.4 | 211.7 | 461.3 | 469.8 | 469.8 | 481.5 |
|----|-------|-------|-------|-------|-------|-------|-------|-------|
| Tp | 189.3 | 199.2 | 209.2 | 212.5 | 461.8 | 470.5 | 470.5 | 482.3 |
| Tp | 190   | 199.9 | 209.9 | 213.3 | 462.4 | 471.1 | 471.1 | 483.1 |
| Tp | 190.7 | 200.6 | 210.7 | 214.1 | 462.9 | 471.8 | 471.8 | 483.8 |
| Tp | 191.3 | 201.3 | 211.4 | 214.8 | 463.5 | 472.5 | 472.5 | 484.5 |
| Tp | 191.9 | 201.9 | 212   | 215.5 | 464.1 | 473.1 | 473.1 | 485.1 |
| Tp | 192.5 | 202.5 | 212.7 | 216.2 | 464.6 | 473.7 | 473.7 | 485.8 |
| Tp | 193.1 | 203.1 | 213.3 | 216.8 | 465.2 | 474.3 | 474.3 | 486.4 |
| Tp | 193.7 | 203.7 | 213.9 | 217.4 | 465.7 | 474.9 | 474.9 | 487  |
| Tp | 194.2 | 204.3 | 214.5 | 218   | 466.3 | 475.5 | 475.5 | 487.6 |
| Tp | 194.8 | 204.8 | 215   | 218.6 | 466.8 | 476.1 | 476.1 | 488.2 |
| Tp | 195.3 | 205.3 | 215.6 | 219.2 | 467.4 | 476.6 | 476.6 | 488.8 |
| Tp | 195.8 | 205.7 | 216   | 219.7 | 467.9 | 477.2 | 477.2 | 489.3 |
| Tp | 196.3 | 206.2 | 216.5 | 220.2 | 468.4 | 477.7 | 477.7 | 489.8 |
| Tp | 196.9 | 206.6 | 216.9 | 220.6 | 469   | 478.2 | 478.2 | 490.4 |
| Tp | 197.4 | 207   | 217.3 | 221   | 469.5 | 478.8 | 478.8 | 490.8 |
| Tp | 197.9 | 207.4 | 217.7 | 221.4 | 470   | 479.3 | 479.3 | 491.3 |
| Tp | 198.4 | 207.9 | 218   | 221.8 | 470.5 | 479.8 | 479.8 | 491.8 |
| Tp | 198.9 | 208.3 | 218.3 | 222.1 | 471.1 | 480.4 | 480.4 | 492.2 |
| Tp | 199.5 | 208.7 | 218.7 | 222.4 | 471.6 | 480.9 | 480.9 | 492.7 |
| Tp | 200   | 209.2 | 219   | 222.7 | 472.1 | 481.4 | 481.4 | 493.1 |
| Tp | 200.5 | 209.6 | 219.3 | 223   | 472.6 | 481.9 | 481.9 | 493.6 |
| Tp | 201   | 210   | 219.6 | 223.3 | 473.3 | 482.5 | 482.5 | 494  |
| Tp | 201.5 | 210.4 | 219.9 | 223.6 | 473.8 | 483.1 | 483.1 | 494.4 |
| Tp | 202.1 | 210.9 | 220.2 | 223.9 | 474.5 | 483.6 | 483.6 | 494.9 |
| Tp | 202.7 | 211.3 | 220.5 | 224.2 | 475.1 | 484.2 | 484.2 | 495.4 |
| Tp | 203.3 | 211.7 | 220.9 | 224.6 | 475.8 | 484.9 | 484.9 | 495.9 |
| Tp | 203.9 | 212.2 | 221.3 | 224.9 | 476.6 | 485.6 | 485.6 | 496.4 |
| Tp | 204.6 | 212.7 | 221.7 | 225.2 | 477.4 | 486.3 | 486.3 | 496.9 |
| Tp | 205.4 | 213.2 | 222.2 | 225.6 | 478.4 | 487.1 | 487.1 | 497.4 |
| Tp | 206.3 | 213.8 | 222.7 | 226   | 479.4 | 488.0 | 488.0 | 498.0 |
| Tp | 207.3 | 214.6 | 223.2 | 226.5 | 480.5 | 489.1 | 489.1 | 498.7 |
| Tp | 208.4 | 215.5 | 223.8 | 227.1 | 481.9 | 490.3 | 490.3 | 499.4 |
| Tp | 209.7 | 216.6 | 224.6 | 227.8 | 483.4 | 491.7 | 491.7 | 500.3 |
| Tp | 211.4 | 218.3 | 225.6 | 228.7 | 485.3 | 493.4 | 493.4 | 501.5 |
| Tp | 213.4 | 220.9 | 227   | 230.1 | 487.5 | 495.3 | 495.3 | 502.9 |
| Tp | 216.3 | 225.5 | 229.3 | 232.4 | 490.4 | 498.4 | 498.4 | 504.9 |
| Tp | 233.0 | 245.5 | 243.8 | 247.6 | 501.8 | 511.8 | 511.8 | 513.2 |

\[ T_p = 470.3 \text{K} \quad T_p = 479.2 \text{K} \quad T_p = 490.1 \text{K} \quad T_p = 494.2 \text{K} \quad T_p = 469.5 \text{K} \quad T_p = 479.1 \text{K} \quad T_p = 488.7 \text{K} \quad T_p = 491.9 \text{K} \]
Figure 2. $E_a$–$\alpha$ curves of catalyzed sample under 4 MPa and 7 MPa obtained by Ozawa's method.

The values of $E_a$ were obtained by Ozawa's method [Eq. (5)] with $\alpha$ changing from 0.01 to 1.00 as shown in table 2. The relations of $E_a$ with $\alpha$ are made in figures. From Fig. 5 and 6 we can see that activation energies of catalyzed sample change little with the increase of conversion degree. In the range of 0.04–0.78 ($\alpha$) under 4 MPa and 0.10–0.84 ($\alpha$) under 7 MPa, activation energies change even faintly, which means that the decomposition mechanism of the processes does not transferred in essence or the transference could be ignored. So, it is feasible to study the reaction mechanism and kinetics in these ranges.

Forty-one types of kinetic model functions in Ref.[14] and the original data (bold italic) tabulated in table 2 are put into $E_{qs},(1)$–(6) for calculations, respectively. The values of $E_a$, $\ln(A/s^{1})$, linear correlation coefficient ($r$) and standard mean square deviation ($Q$) under 4 MPa and 7 MPa can be calculated on the computer with the linear least squares method on various heating rates of 5, 10, 20 and 25 K-min$^{-1}$ are listed in table 3. The most probable mechanism function is selected by the better values of $r$, and $Q$ based on the following four conditions: (1) the values of $E_a/(kJ•mol^{-1})$ and $\ln(A/s^{1})$ selected are in the ordinary range of the thermal decomposition kinetic parameters for solid materials [$E_a/(kJ•mol^{-1})=80–250$ and $\ln(A/s^{1})=7–30$]; (2) linear correlation coefficient ($r$) is greater than 0.98; (3) the values of $E_a/(kJ•mol^{-1})$ and $\ln(A/s^{1})$ obtained with the differential and integral methods are approximately the same; (4) the mechanism function selected must be in agreement with the tested sample state. The results of satisfying the conditions mentioned above are listed in table 3.

Table 3. Kinetic parameters for the decomposition process of catalyzed sample under 4 and 7 MPa.

| Method       | $\beta$ (K•min$^{-1}$) | $E_a$ (kJ•mol$^{-1}$) | $\ln(A/s^{1})$ | $r$   | $Q$       | $E_a$ (kJ•mol$^{-1}$) | $\ln(A/s^{1})$ | $r$   | $Q$       |
|--------------|------------------------|-----------------------|-----------------|-------|-----------|-----------------------|-----------------|-------|-----------|
| Ordinary     | 5                      | 133.2                 | 13.2            | 0.9978| 0.0559    | 135.5                 | 12.8           | 0.9935| 0.2256    |
|              | 10                     | 142.8                 | 13.6            | 0.9997| 0.0077    | 131.7                 | 12.4           | 0.9986| 0.0497    |
|              | 20                     | 144.3                 | 13.7            | 0.9976| 0.0605    | 131.7                 | 12.7           | 0.9986| 0.0497    |
|              | 25                     | 141.2                 | 13.4            | 0.9973| 0.065     | 136.9                 | 13.0           | 0.9992| 0.0281    |
| Mac          | 5                      | 139.3                 | 13.2            | 0.9980| 0.0104    | 135.6                 | 12.8           | 0.9943| 0.0422    |
| Callum       |                         |                       |                 |       |           |                       |                 |       |           |
| -Tanner      |                         |                       |                 |       |           |                       |                 |       |           |
The values of $E_a$(kJ•mol$^{-1}$) and $\lg(A/s^{1})$ obtained from a single non-isothermal DSC curve are in good agreement approximately with the values calculated by Kissinger's method and Ozawa's method. Therefore, we conclude that the reaction mechanism of the main exothermal decomposition process of the sample under 4 MPa and 7 MPa are the same one. It is classified as random nucleation and then growth, and the mechanism function is the Avrami-Erofeev Equation with $n=$2/3, and $G(\alpha) = \left[-\ln(1-\alpha)\right]^{2/3}$, $f(\alpha) = (3/2)(1-\alpha)[-\ln(1-\alpha)]^{1/3}$. Substituting $f(\alpha)$ with $(3/2)(1-\alpha)[-\ln(1-\alpha)]^{1/3}$, $E_a$/kJ•mol$^{-1}$ with 142.1 and $\lg(A/s^{1})$ with 13.5 into Eq.(7)

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-E_a/RT} \quad (7)$$

The kinetic equation of exothermal decomposition reaction under 4 MPa may be described as:

$$\frac{d\alpha}{dt} = 10^{13.7} \left(1-\alpha\right)\left[-\ln(1-\alpha)\right]^{1/3} e^{-17091.6/T} \quad (8)$$

Substituting $f(\alpha)$ with $(3/2)(1-\alpha)[-\ln(1-\alpha)]^{1/3}$, $E_a$/kJ•mol$^{-1}$ with 134.2 and $\lg(A/s^{1})$ with 12.7 into Eq.(7). The kinetic equation of exothermal decomposition reaction under 7 MPa may be described as:

$$\frac{d\alpha}{dt} = 10^{12.8} \left(1-\alpha\right)\left[-\ln(1-\alpha)\right]^{1/3} e^{-16141/A/T} \quad (9)$$

The calculated kinetic parameters of catalyzed propellants and the kinetic parameters of non-catalyzed basic samples reported in reference [8] are listed in table 4. According to the comparison of parameter data, at the same test pressure, the activation energies and pre-exponential factors of the reaction of catalytic HNIW-CMDB propellants are different from that of the non-catalyzed samples, but the mechanism function of the reaction are the same one. The main exothermic decomposition process is the Avrami-Erofeev equation ($n=$2/3). It can be concluded that, the burning rate catalyst B-Pb can change the reaction rate of the basic samples without changing the reaction mechanism, that means, the reaction stability of the basic samples.
Table 4. Kinetic parameters and mechanism function for the decomposition process of basic sample and catalyzed sample under 4 and 7 MPa.

| No.         | P/MPa | Mechanism function | $E_a/(kJ\cdot mol^{-1})$ | $lg(A/s^{-1})$ |
|-------------|-------|--------------------|--------------------------|----------------|
| non-catalyzed sample | 4     |                    | 149.5                    | 14.3           |
| non-catalyzed sample | 7     | $G(a)=[-\ln(1-\alpha)]^{1/2}, f(\alpha)=3/(2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$ | 150.8          | 14.5           |
| catalyzed sample    | 4     | Avrami-Erofeev, $n=2/3$ | 142.1                    | 13.5           |
| catalyzed sample    | 7     |                    | 134.2                    | 12.7           |

4. Conclusions

(1) At atmospheric pressure, there are two obvious exothermic peaks on the DSC curve of catalytic HNIW-CMDB propellants, and at high pressure, the catalytic propellants exhibit an obvious exothermic peak, and the peak temperature decreases with the increase of heating rate.

(2) When the catalyst B-Pb is added to the sample, the activation energy and pre-exponential factor of HNIW-CMDB propellants will not be changed. The reaction mechanism of the samples is not affected by the pressure. The mechanism functions of the catalytic and non-catalytic reactions under different pressures are the Avrani-Erofeev equation ($n=2/3$).

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