IOP Conf. Series: Earth and Environmental Science **108** (2018) 022016 doi:10.1088/1755-1315/108/2/022016

Study on Thermal Decomposition Characteristics of Two Kinds of Propellant

Yongkang Chen[1], Zhentao An[1], Minghua Chen[2] and Li Zhang[1]

[1]Shijiazhuang Campus of Army Engineering University, Shijiazhuang 050003, China
[2]Mechanical Technology Research Institute, Shijiazhuang 050003, China

*Corresponding author e-mail: sharpions@126.com

Abstract. In order to study the thermal decomposition characteristics of modified double-base propellant and cobalt-2 double-base propellant, their thermal decomposition process were tested with accelerating rate calorimeter(ARC). Thermal decomposition characteristic parameters were obtained by analyzing temperature-time curves, pressure-time curves and temperature rate-time curves. The kinetic parameters were calculated by velocity constant method. It is showed that the initial exothermal temperature of modified double base propel-lant is 134.8℃, E=185 kJ•mol^{-1}. The initial exothermal temperature of cobalt-2 double-base propellant is 125.3 ℃ , E=144.9J•mol^{-1}. It means that the thermal stability of these two kinds of propellant are fine and the stability of modified double-base propellant is better.

1. Introduction

At present, modified double-base propellant and cobalt-2 double base propellant has been widely used in some rocket engine. The study of the thermal stability of these two kinds of propellants has not been seen much. In the study of energetic material thermal decomposition properties and thermal stability, thermogravimetry (TG) [1], differential thermal analysis (DTA) [2]and differential scanning calorimetry (DSC) [3] methods are commonly used. But the quantity of sample using in these testing methods is only a few milligrams, test results are difficult to be representative, furthermore pressure in decomposition process cannot be measured by these methods. Accelerating rate calorimeter can make up for this deficiency. In this paper, thermal decomposition process of these two kinds of propellants was studied by accelerating rate calorimeter to calculate the kinetic parameters and determine their stability.

2. Test Part

2.1. Sample preparation

The experimental sample is modified double-base propellant and cobalt-2 double-base propellant.

2.2. Instruments and Test Conditions

The experimental instrument is accelerating rate calorimeter produced by British Thermal Hazard Technology Company (THT). Sample containers are thick titanium alloy ball (Ti-LCQ). The amount of sample and test conditions is in Table 1.

Table 1. Mass of samples and measuring conditions.

m/mg	m_b/g	$\overline{C_{v,b}}$ /J·g^{1}℃	T_{start}/℃	T_{step}/℃	t_{wait}/min	s/℃•min^{-1}
32.4	8.5122	0.42	70	5	15	0.020
244	8.5122	0.42	70	5	15	0.020

m_b is the mass of sample ball; T_{start} is the initial temperature; t_{wait} is waiting time; s is the temperature rising rate sensitivity

3. Results and discussion

3.1. The Adiabatic Decomposition of Two Propellants

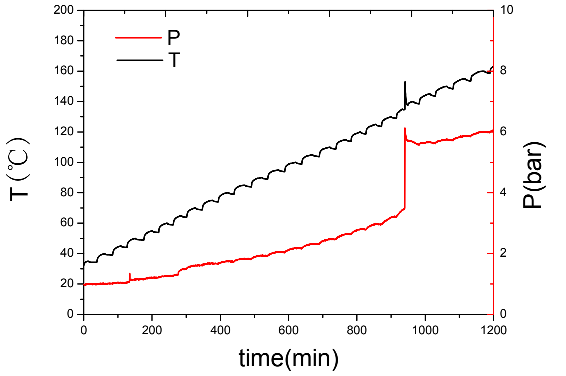

Figure 1. T and P vs. time curve of modified propellant.

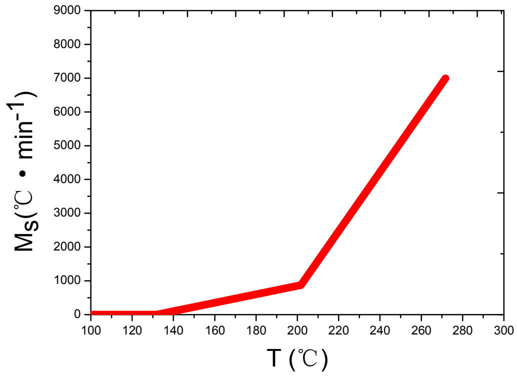

Figure 2. T rate vs. time curve of modified propellant.

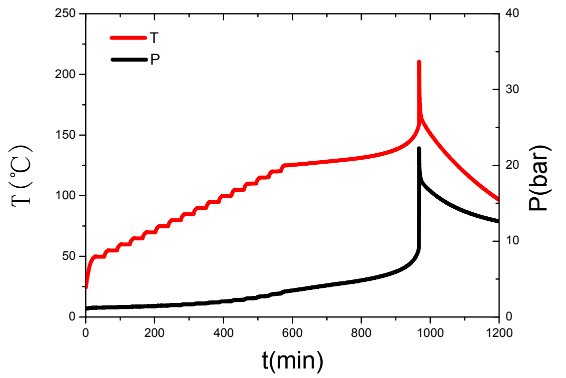

Figure 3. T and P vs. time curve of cobalt-2 propellant.

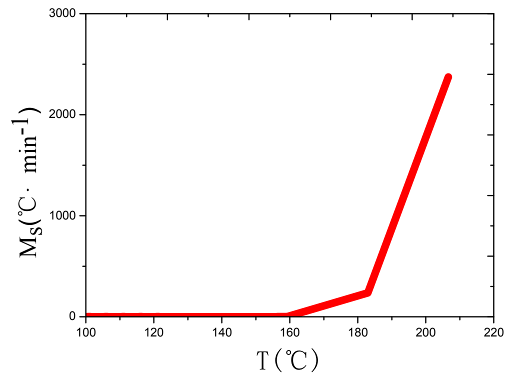

Figure 4. T rate vs. time curve of cobalt-2 propellant.

According to the experimental results of thermal decomposition curves, the characteristic parameters of the thermal decomposition of the sample can be determined. It is showed in Table 2.

Table 2. Thermal decomposition characteristic data of propellant.

$T_{0,s}$/℃	$T_{f,s}$/℃	$T_{m,s}$ /℃	$\Delta T_{ad,s}$/℃	$P_{m,s}$/bar	$M_{0,s}$/℃•min^{-1}	$M_{m,s}$/℃•min^{-1}
134.8	152.93	152.93	18.1	6.190	0.033	6994.14
125.3	211.0	211.0	85.7	21.297	0.024	2157.6

$T_{0,s}$ is the system of initial decomposition temperature; $T_{f,s}$ is the system terminating reaction temperature; $T_{m,s}$ is the system's maximum decomposition rate of temperature; $\Delta T_{ad,s}$ is system for the adiabatic temperature rise; $P_{m,s}$ is the largest reaction pressure; $M_{0,s}$ as the system initial decomposition rate; $M_{m,s}$ is the system maximum decomposition rate.

From Table 2 that the initial decomposition temperature modified double base propellant is 134.8℃, the maximum pressure is 6.19bar, the maximum temperature rise rate is 6994.14℃•min^{-1}. The initial decomposition temperature of cobalt-2 double base propellant is 125.3℃, the maximum pressure is 21.3bar, the maximum temperature rise rate is 2157.6℃•min^{-1}. The initial decomposition temperature modified double base propellant is higher than cobalt-2 double base propellant. It shows that the thermal stability of modified double base propellant is superior to the cobalt-2 double base propellant. From the temperature curve, the gradually exothermic decomposition process of cobalt-2 double base propellant is significantly slower than modified double base propellant. From the pressure curve, after the start of exothermic decomposition, decomposition of cobalt-2 double base propellant slowly began, and it releases a small amount of gas, which resulting in pressure increasing gradually. The process of modified double-base propellant is a quite rapid process of combustion and explosion. It shows that the decomposition rate of modified double-base propellant is faster than the double cobalt-2 double base propellant.

3.2. Corrected testing parameters

The heat produced by samples in the decomposition process is not fully used for heating itself. There are part of the heat absorbed by the container ball making the temperature rising. The temperature measured in the test is not the temperature of the sample but the system. So we need to introduce thermal inertia factor Φ to make the test results more accurate [4, 5].

$$\phi = \frac{(m\overline{C_v} + m_b\overline{C_{v,b}})}{m\overline{C_v}} \tag{1}$$

In the formula, ΔT_{ad} is adiabatic temperature rise of sample,

$$\Delta T_{ad,s} = \frac{\Delta T_{ad}}{\phi} \tag{2}$$

The initial exothermic temperature for the sample,

$$T_0 = \left(\frac{1}{T_{0,s}} + \frac{R}{E_a}\ln\phi\right) \tag{3}$$

The heat release end temperature of the sample:

$$T_f = T_0 + \Delta T_{ad} \tag{4}$$

The testing results modified by Φ are showed in Table 3.

Table 3. Thermal decomposition characteristic data modified by Φ.

sample	Φ	T_0/℃	T_f/℃	ΔT_{ad}/℃	M_0/℃•min-1	M_m/℃•min^{-1}
modified	8.61	132.72	288.81	156.10	0.28	63221.8
cobalt-2	7.16	124.0	738.5	613.2	0.172	15437.6

M_0 is the initial sample decomposition rate; M_m is the sample maximum decomposition rate.

3.3. *Thermal Decomposition Kinetics Parameters*

Based on the adiabatic temperature rise equation:

$$m_{T,s} = \frac{dT}{dt} = k\left(\frac{T_{f,s} - T_s}{\Delta T_{ad,s}}\right)^n \Delta T_{ad,s} \quad (5)$$

$$\ln k = \ln\left(\frac{m_{T,s}}{\left(\frac{T_{f,s} - T_s}{\Delta T_{ad,s}}\right)^n \Delta T_{ad,s}}\right) \quad (6)$$

The Arrhenius formula is the logarithm to both sides [6]:

$$\ln k = \ln A - \frac{E}{R} \cdot \frac{1}{T} \quad (7)$$

Through the ARC test $m_{T,s}$, $T_{f,s}$ and $\Delta T_{ad,s}$ are obtained. When the reaction series is suitable, Ink obtainted in Formula (6) will be calculated into Formula (7). Take $1/T$ as the abscissa axis, take Ink as the ordinate axis for linear fitting. The activation energy is calculated by the slope, the pre-exponential factor is calculated by intercept.

In the intense exothermic reaction, the assumption is that the reactant concentration is unchanged. In this way the reaction order is 0. The thermal dynamic parameters of the sample are calculated by data fitting.

Table 4. Thermal decomposition characteristic data modified by Φ.

sample	E/kJ•mol^{-1}	A/s$^{-1}\times10^{15}$
modified	185.0	8.6
cobalt-2	144.9	7.8

4. Conclusion

Initial decomposition temperature of modified double base propellant is 134.8℃. The maximum speed of the decomposition temperature is 152.9℃. The initial decomposition temperature after corrected is 132.72℃. The maximum temperature rise rate is 6994.14℃•min^{-1}. Activation energy E=185kJ•mol^{-1}, pre-exponential factor A=8.6×10^{8}s^{-1}. Initial decomposition temperature of cobalt-2 double base propellant is 125.3℃. The maximum speed of the decomposition temperature is 211℃. The maximum temperature rise rate is 2157.6℃•min^{-1}. Activation energy E=144.9kJ•mol^{-1}, pre-exponential factor A=7.8×10^{8}s^{-1}. The decomposition temperature and activation energy show that these two kinds of propellant have good thermal stability. At the same time, the initial decomposition temperature and activation energy modified double base propellant are higher than that of cobalt-2 double base propellant. It shows that the thermal stability of modified double base propellant is superior to cobalt-2 double base propellant. The decomposition rate of modified double base propellant is faster than the double cobalt-2 double base propellant.

References

[1] Wang Ji. Study on Thermal Characteristics of Ammonium Nitrate After Long-term Storage [J]. Science & Technology Review, 2012, 30 (1): 60-64.
[2] FU Zhi-min. Evaluating thermal stability for reactive chemical by accelerating rate calorimeter [D]. Beijing: School of Mechana-Electronics Engineering, Beijing Institute of Technology, 2002.
[3] Zeng Xiu-Lin. Experimental and Theoretical Studies on the Thermal Stability of Nitrates [D]. Nanjing: Nanjing University of Science and Technology, 2007.
[4] GUO Hong. Application of accelerating rate calorimeter (ARC) to the thermoanalytic study on dynamics mechanism [J]. Journal of Qujing Teachers College, 2005, 24 (3): 1-3.
[5] Hu Rongzu, Gao Shengli, Zhao Fengqi et al. Thermal Analysis Kinetics[M]. Beijing: Science Press, 2008.
[6] ZHOU Xin-li, LIU Zu-liang, LÜ Chun-xu. Adiabatic decomposition of No.3 permissible expanded ammonium nitrate explosive [J]. Chinese Journal of Explosives & Propellants, 2007, 30 (5): 15~18.