Available online at www.sciencedirect.com
SCIENCE DIRECT
Thermochimica Acta 416 (2004) 75–78
thermochimica acta
www.elsevier.com/locate/tca

Effect of ballistic modifiers on thermal decomposition characteristics of RDX/AP/HTPB propellant

Feng-Qi Zhao [a,b,*], Pei Chen [b], Shang-Wen Li [b]

[a] *Shaanxi Key Laboratory of Physica-Inorganic Chemistry, Department of Chemistry, Northwestern University, Xi'an 710069, China*
[b] *Xi'an Modern Chemistry Research Institute, Xi'an 710065, China*

Received 30 October 2002; received in revised form 30 November 2002; accepted 30 December 2002

Available online 16 January 2004

Abstract

The effects of different ballistic modifiers ($Cr_2O_3{\cdot}CuO$, ammonium oxalate, and carbon fiber) on the thermal decomposition behavior of RDX/AP/HTPB propellant are studied using pressure DSC. The burning rates of the four propellants are determined by using a Crawford bomb. The results show that in the presence of $Cr_2O_3{\cdot}CuO$ or carbon fiber, the peak temperatures of the decomposition of RDX and AP decrease. The enthalpy of decomposition and the burning rates and the number of the exothermic decomposition peak of two kind of RDX/AP/HTPB propellant containing $Cr_2O_3{\cdot}CuO$ and carbon fiber increase. When ammonium oxalate is added into the RDX/AP/HTPB system, the peak temperature of decomposition of RDX shifts upwards, and the enthalpy of decomposition of RDX/AP/HTPB propellant decreases, and the burning rate reduces. These facts indicate that the relationship between the effect of the ballistic modifiers on the burning rate and that on the thermal behavior of RDX/AP/HTPB propellant is close.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Ballistic modifiers; Burning rate; Pressure DSC; RDX/AP/HTPB propellant; Thermal decomposition

1. Introduction

RDX/AP/HTPB propellant has the advantages of high energy and reduced smoke. It has been showed that this propellant has a critical shortcoming of lower burning rate, which implies that it is necessary to look for ballistics modifiers to improve its burning rate. In the research area of improving the burning rate of this propellant, Zhao et al. studied the combustion characteristics and thermal behavior of AP and RDX [1–4]. Seldom, however, have the thermal decomposition of RDX/AP/HTPB propellant and the effect of ballistic modifiers on the burning rate of RDX/AP/HTPB propellant been reported. In this paper, we report the studies on the of $Cr_2O_3{\cdot}CuO$, ammonium oxalate and carbon fiber on the thermal decomposition characteristics and the burning rate of RDX/AP/HTPB propellant by means of PDSC. This is quite useful for the selection of ballistics modifiers and the study of relativity between the thermal decomposition characteristic and the burning rate of RDX/AP/HTPB propellant.

* Corresponding author.
E-mail address: npecc@21cn.com (F.-Q. Zhao).

2. Experimental

2.1. Materials

$Cr_2O_3{\cdot}CuO$ and ammonium oxalate used in this study were prepared in Xi'an Modern Chemistry Research Institute. Cyclotrimethylenetrinitramine (RDX) was purchased from Baiyin Chemical Engineering Factory. Hydroxy terminated polybutadiene (HTPB), ammonium perchlorate (AP), aluminium power and carbon fiber were commercial products. Four propellants used were prepared by a vacuum cast technique. Their compositions were listed in Table 1.

2.2. Equipment and experiment condition

The DSC experiments were carried out on a model DSC190S instrument (TA Co., USA). The condition of DSC were as follows: sample mass, less than 2.00 mg; heating rate, 10 °C min^{-1}; pressure, 0.1, 3, 5 MPa; atmosphere, a flowing rate of N_2 gas of 50 ml min^{-1}. The burning rates of the four propellants were determined by using a Crawford bomb. The results were shown in Table 2.

0040-6031/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2003.11.034

Table 1
Compositions of RDX/AP/HTPB propellant

Sample	Composition	Mass ratio
1	HTPB/AP/RDX/Al	10:60:20:5
2	HTPB/AP/RDX/Al/Cr_2O_3·CuO	10:60:20:5:5
3	HTPB/AP/RDX/Al/ammonium oxalate	10:60:20:5:5
4	HTPB/AP/RDX/Al/carbon fiber	10:60:20:5:5

Table 2
The burning rate characteristics of RDX/AP/HTPB propellant

Sample	Burning rate at different pressure (MPa) (mm s^{-1})					Pressure exponent at 8–10 MPa
	2	4	6	8	10	
1	4.10	5.27	6.23	7.02	7.42	0.26
2	5.75	7.80	9.79	11.10	11.79	0.25
3	4.12	4.33	4.95	5.29	5.50	0.17
4	30.60	48.22	60.06	68.55	72.48	0.26

3. Results and discussion

3.1. Thermal decomposition characteristics of the control composition at different pressures

DSC curves of sample 1 at different pressures are shown in Fig. 1. It can been seen form Fig. 1 that under 0.1 MPa, the endothermic peak at 203.6 °C is due to the phase change from solid to liquid of RDX. Two-minute exothermic peaks at 213.4 and 240.2 °C are caused by the decomposition reaction of HTPB and RDX, respectively. The minute endothermic peak at 244.6 °C is due to the crystal transformation of AP and the stronger exothermal peak at 371.4 °C is caused by the decomposition reaction of AP. With increasing the pressure, the minute exothermic peak of HTPB decomposition is gradually covered with the exothermic peak of RDX decomposition. The enthalpies of decomposition of RDX and AP increase obviously. The decomposition temperature of RDX is constant basically. The decomposition temperature of AP shifts to higher temperature and the peak shape becomes more and more complication. The decomposition temperature of AP under 3 MPa is higher than that under 5 MPa.

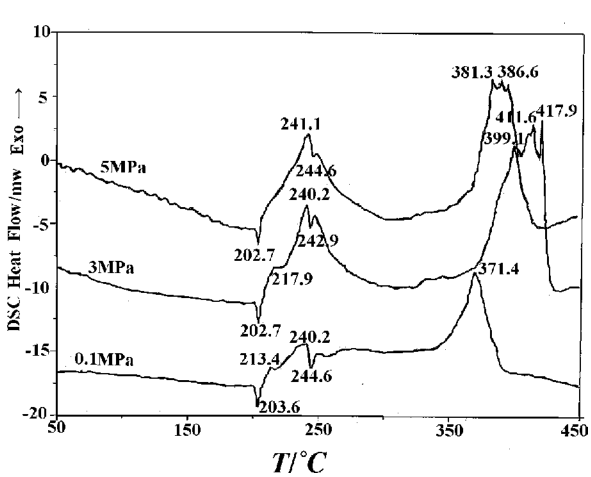

Fig. 1. DSC curves of sample 1.

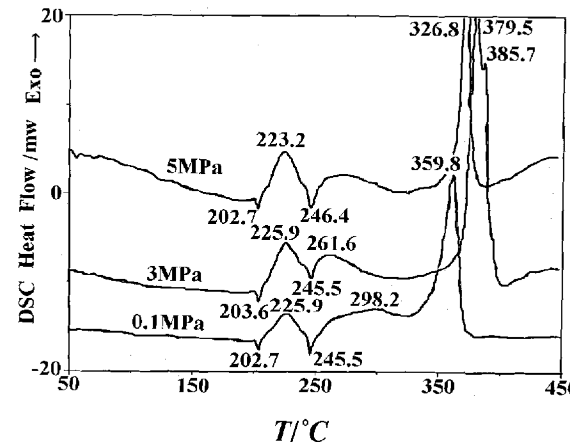

Fig. 2. DSC curves of sample 2.

3.2. Thermal decomposition characteristics of the propellant containing Cr_2O_3·CuO

DSC curves of sample 2 at different pressure are shown in Fig. 2. By comparing Fig. 1 with Fig. 2, the following observations on the thermal decomposition characteristics of RDX/AP/HTPB propellant in the presence of Cr_2O_3·CuO may be obtained:

(1) The minute exothermal peak of HTPB at 213.4 °C in Fig. 1 disappears in Fig. 2.
(2) At 0.1 MPa, the decomposition temperature of AP in sample 2 declines from 371.4 to 359.8 °C, and that of RDX declines from 240.2 to 225.9 °C.
(3) An exothermic peak appeared at 298.2 °C is due to the decomposition of AP at lower temperature. With increasing the pressure, this peak is shifted downward.
(4) The shape of decomposition peak of AP at higher temperature becomes very sharp, which refers that the decomposition rate of AP increases.
(5) There is no distinct peak valley from the decompositions of RDX at 225.9 °C to the decomposition of AP at 298.2 °C, until the decomposition of AP at 359.8 °C, which shows RDX/AP/HTPB propellant released heat steadily in the presence of Cr_2O_3·CuO. This result is very useful in increasing the burning rate of propellant.

3.3. Thermal decomposition characteristics of the propellant containing ammonium oxalate

Comparing DSC curves of sample 3 in Fig. 3 with that of the control propellant in Fig. 1, we find that the melting peak of RDX at 203.6 °C disappears. The decomposition peak of RDX emerges after the crystal transformation peak of AP,

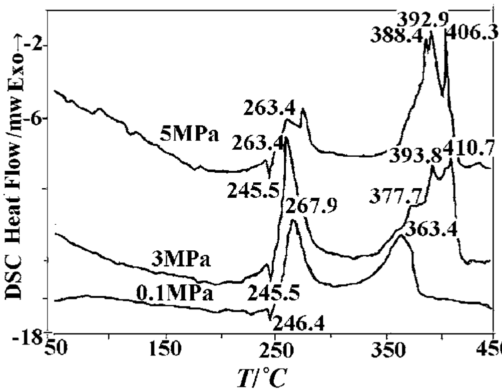

Fig. 3. DSC curves of sample 3.

and its decomposition temperature goes up from 240.0 to 267.9 °C. When the pressure increases to 5 MPa, the decomposition peak of RDX becomes smaller, and the heat of decomposition of RDX decreases. The peak temperature of decomposition of AP becomes lower, and the heat of AP decomposition decreases. These results show that ammonium oxalate restrains the decompositions of RDX and AP. The burning rate of sample 3 containing ammonium oxalate decreases.

3.4. Thermal decomposition characteristics of the propellant containing carbon fiber

Comparing DSC curve of sample 4 containing carbon fiber in Fig. 4 with the DSC curves of the control propellant in Fig. 1, we find that there is an exothermic peak at 187.5 °C before melting peak of RDX. It is due to the decomposition of HTPB. With increasing the pressure, the peak temperature shifts to higher temperature, and the peak temperature under 3 MPa is close to that under 5 MPa. The peak temperature of the exothermal decomposition of HTPB shifts toward lower temperature and close to the exothermic peak temperature of AP gradually. This results in putting the exothermic process

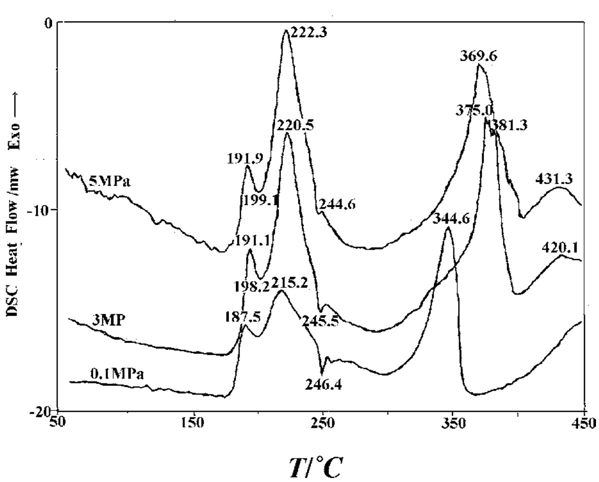

Fig. 4. DSC curves of sample 4.

Table 3
Enthalpy of the decomposition of RDX/AP/HTPB propellant

Sample	ΔH_d (J g^{-1})		
	0.1 MPa	3 MPa	5 MPa
1	295.9	269.9	381.9
2	458.2	598.8	577.1
3	113.0	167.6	142.0
4	1274	1660	1856

of sample 4, which is very beneficial to increase the burning rate.

In sample 4 containing carbon fiber, the exothermic decomposition peak temperature of RDX and AP decreases to 215.2 and 344.6 °C, respectively. The exothermic decomposition rate and the heat of decomposition of RDX increase clearly. So the burning rate of sample 4 containing carbon fiber is highest.

3.5. The relativity between the combustion catalysis effect of ballistic modifiers and the thermal decomposition characteristic of RDX/AP/HTPB propellant

With the peak temperature of decomposition of RDX or AP shifting to lower temperature, the burning rate of propellant increases. From Figs. 2–4 and Table 2, we can see that the peak temperature of the decomposition of RDX and AP in sample 4 containing carbon fiber is lowest and accordingly the burning rate of sample 4 is fastest. For sample 2 containing $Cr_2O_3{\cdot}CuO$, the peak temperature of AP is higher than that in sample 4, but the peak temperature of RDX is lower about 40 °C than that in sample 3. So the burning rate of sample 2 is higher than that of sample 3. For sample 3 containing ammonium oxalate, the peak temperature of AP decomposition (363.4 °C) is highest in three propellants. Hence, the burning rate of sample 3 is lowest. These facts show that the decomposition temperature of component is related to the burning rate of propellant.

DSC curve of sample 4 containing carbon fiber shows that an exothermic peak of HTPB at 187.5 °C before the melting peak of RDX. However, this phenomenon does not exist in DSC curves of samples 2 and 3. In comparison with samples 2 and 3, the burning rate of sample 4 is the fastest, indicating that lower the exothermic peak temperature of main component in propellant is, higher the burning rate of propellant.

Setting the decomposition course before the crystal transformation peak of AP at 245 °C as the onset decomposition process of RDX/AP/HTPB propellant, and the global area under the exothermic peaks corresponding to this course as the enthalpies of the decomposition (ΔH_d) of samples 1–4, the values of ΔH_d in Table 3 are obtained. It is clearly seen from Table 3 that in the study pressure range (0.1–5 MPa), both $Cr_2O_3{\cdot}CuO$ and carbon fiber make the (value of ΔH_d) increase. The value of ΔH_d of sample 4 is larger than that of ΔH_d of sample 2. This shows that the effect of carbon fiber is more outstanding. But ammonium oxalate makes the enthalpy of decomposition decrease. Above-mentioned facts show that the enthalpy of decomposition of propellant is related to the burning rate of propellant, and the more the onset decomposition heat is, the higher the burning rate of propellant.

The thermal decomposition process of sample with carbon fiber has four close-linked exothermic decomposition stages: the exothermic reaction of HTPB at lower temperature, the exothermic decomposition reaction of RDX and the exothermic decomposition reactions of AP and HTPB at higher temperature. The burning rate of sample 4 is the fastest. The thermal decomposition process of sample 2 with $Cr_2O_3 \cdot CuO$ has three exothermic stages: the exothermal decomposition reaction of RDX and the exothermic decomposition reaction of AP at lower and higher temperature. However, the decomposition process of sample 3 with ammonium oxalate has only two exothermic decomposition stages: the exothermic decomposition reactions of RDX and AP. The burning rate of sample 3 is the lowest. These facts indicate that there is a correlation between the number of exothermic stages and the burning rate of propellants with different ballistic modifiers.

References

[1] F.-Q. Zhao, D. Yang, Z. Dang, in: Proceedings of the 26th Internation Pyrotechnics Seminar, IPS, Nanjing, Nanjing University of Science and technology, October 1–4, 1999, p. 634.
[2] L. Li, F.-Q. Zhao, S.-W. Li, Y. Su, C. Dong, Chin. J. Explosive Propell. 19 (3) (1997) 11.
[3] S. Liu, F.-Q. Zhao, S.-W. Li, Chin. J. Explosive Propell. 2 (1998) 33.
[4] Z. Liu, C. Yin, Y. Kong, F.-Q. Zhao, J. Solid Rocket Technol. (China) 25 (3) (2002) 45.