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BTATz-CMDB propellants

High-pressure thermal properties and their correlation with burning rates

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Abstract The high-pressure thermal properties and their correlation with burning rates of the composite modified double base (CMDB) propellants containing 3,6-bis (1H-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (BTATz), a substitute of hexogen (RDX), were investigated using the high-pressure differential scanning calorimetry (PDSC). The results show that there is a main exothermal decomposition process with the heating of each propellant. High pressure can restrain the volatilization of NG, accelerate the main decomposition reaction, and make the reaction occur easily. High pressure can change the main decomposition reaction mechanism function and kinetics, and the control process obeys the rule of Avrami–Erofeev equation at high pressure and chemical reaction at normal pressure. However, the mechanism function can not be changed by the ballistic modifier. The correlation between PDSC characteristic values and burning rates was carried out and found that u and $(p\,\Delta H_{\mathrm{d}}/\Delta T)^{1/2}$ keep a good linear relation, k_u keeps a similar changing trend with u, and it can be used to study the effect of the ballistic modifier or the other component on the burning rates.

Keywords BTATz-CMDB propellant · High pressure · Thermal property · Burning rate · Correlation

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Introduction

Because of the large positive enthalpy of formation, insensitivity to impact, friction and electrostatic discharge, and low-molecular-weight reaction products, the high-nitrogen energetic compounds have a prospect application as one of the important components for the solid rocket propellants [1–6]. 3,6-Bis(1H-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (BTATz) is one of such materials, and be thought as a substitute of hexogen (RDX) in the composite modified double base (CMDB) propellant with the high burning rate and favorable combustion property [7–10].

The BTATz-CMDB propellants without and with the ballistic modifier were prepared, and the investigation at normal pressure was carried out in our preceding study [11]. However, the results obtained by normal-pressure method are not a close match with high-pressure one after all. In this study, the high-pressure differential scanning calorimetry (PDSC) analysis was carried out to research the thermal properties and their correlation with burning rates of the BTATz-CMDB propellants at high pressures, which are close to the work condition of the solid propellant charged in the rocket motor. It is the high-pressure method that deduces to the innovation of the article, and this study has not been found in literatures [12, 13].

Experimental

Materials

The samples used in the experiment are two BTATz-CMDB propellants RB0601 and RB0602, the same as in Ref. [11], composed of 38% (mass fraction) nitrocellulose (NC), 28% nitroglycerin (NG), 26% BTATz, 8%

N-nitro-dihydroxyethylamine-dinitrate (DINA), and other auxiliary. The strand samples of RB0601 composed of 500 g ingredients without ballistic modifier, and RB0602 composed of 500 g ingredients with 17.5 g the mixture of lead phthalate, copper adipate and carbon black as a ballistic modifier were prepared by a solventless CMDB propellant extrusion technique.

Equipment and conditions

PDSC curves were obtained using a Netzsch 204HP high-pressure differential scanning calorimeter, and the conditions were: nitrogen gas purity, 99.999%; flowing rate, 50 cm^3 min^{-1}; sample mass, about 1 mg; heating rate (β), 5, 10, 15, 20, 25, and 30 K min^{-1}; reference sample, α-Al_2O_3; type of crucible, aluminum pan with a pierced lid.

Results and discussion

PDSC analysis

The PDSC curves for the propellants RB0601 and RB0602 at a heating rate of 10 K min^{-1} are shown in Fig. 1, and the basic data for the main exothermic decomposition processes are listed in Table 1. From them, one can find that there are two exothermic peaks in a DSC curve, the main exothermal process attributes to the decomposition of NG, DINA, NC, and other auxiliary, and the subordinate one attributes to that of BTATz [11–13]. Assuming the decomposition reaction of the propellants occur with the increase in pressure at one of the heating rates, the peak temperature of the main exothermic process decreases, the initial temperature and the decomposition heat keeps a rising trend and the terminal temperature keeps a decreasing trend, making the main exothermic peak become accurate and gangling, the reason may be that high pressure restrains the volatilization of NG and accelerates the decomposition reaction, making the system release more heat. Furthermore, high pressure makes the decomposition peak temperature of BTATz at 7 MPa disappear, and this may be that high pressure and exothermic effect make the tetrazole and tetrazine rings in BTATz molecule break easily at a relatively low temperature [6, 14].

Decomposition reaction kinetics calculation

The PDSC curves of the propellants RB0601 and RB0602 at the pressure of 0.1, 4, and 7 MPa and the heating rate of 5, 10, 15, 20, 25, and 30 K min^{-1} were dealt with mathematic means, and the temperature data corresponding to the conversion degrees (α) were obtained.

Five integral methods (General integral, Mac Callum–Tanner, Šatava–Šesták, Agrawal, Ozawa) and one differential method (Kissinger) were employed to calculate the corresponding kinetic parameters [apparent activation energy (E_a/kJ mol^{-1}), pre-exponential constant (A/s^{-1})] and the most probable kinetic model functions [11–13, 15–18]. The values of E_a were obtained by Ozawa's method from the isoconversional DSC curves, and the E_a–α relations are shown in Fig. 2. From one curve in Fig. 2, one can see that the activation energy changes slightly in a proper section of conversion degree for one of the curves, and the section was selected to calculate the nonisothermal reaction kinetics.

Forty-one types of kinetic model functions and the basic data for one propellant were put into the integral and differential equations for calculation, the values of E_a, A/s^{-1}, and the linear correlation coefficient (r) were calculated on computer with the linear least-squares method, and the most probable mechanism function is selected by the better values of r and Q [11–13, 15–18]. The results of satisfying the conditions at the same time are the final results as listed in Tables 2 and 3, and the relevant function is the reaction mechanism function of the decomposition process.

From Tables 2 and 3, one can find that the values of E_a and A obtained from the nonisothermal DSC curves are in approximately good agreement with the values calculated by Kissinger's method and Ozawa's method, and the decomposition reaction mechanism functions of the propellants are listed in Table 4. Respectively, substituting

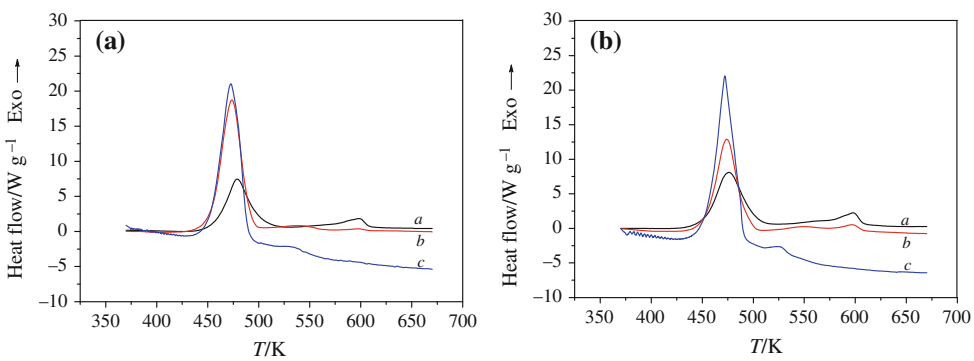

Fig. 1 PDSC curves for the propellants RB0601 (**a**) and RB0602 (**b**) at a heating rate of 10 K min^{-1} Pressure (MPa): (*a*): 0.1; (*b*): 4; (*c*) 7

Table 1 The characteristic data of PDSC for the propellants RB0601 and RB0602

Sample	P/MPa	β/K min^{-1}	T_0/K	T_e/K	T_p/K	T_f/K	ΔT/K	ΔH_d/ 10^3 J g^{-1}
RB0601	0.1	5	415.5	449.7	471.4	519.5	104.0	1.55
		10	426.2	456.0	476.9	530.5	104.3	1.45
		15	430.1	458.0	480.5	533.6	103.5	1.57
		20	431.5	460.8	483.6	536.7	105.2	1.63
		25	432.9	463.3	485.6	543.4	110.5	1.59
		30	434.1	465.8	488.6	544.1	110.0	1.46
	4	5	422.8	446.1	467.0	497.2	74.4	2.62
		10	430.8	454.1	473.7	502.2	71.4	2.63
		15	432.3	455.5	478.6	510.2	77.9	2.78
		20	436.7	461.9	481.4	511.3	74.6	2.63
		25	442.1	463.0	485.4	511.4	69.3	2.57
		30	443.1	464.8	487.2	513.4	70.3	2.81
	7	5	423.2	450.2	467.4	494.7	71.5	2.98
		10	428.1	453.4	475.8	497.9	69.8	3.10
		15	431.1	459.8	478.5	504.2	73.1	3.36
		20	439.4	463.2	483.2	508.2	68.8	2.71
		25	443.8	465.5	486.4	511.2	67.4	3.25
		30	450.5	468.2	488.7	509.0	58.5	2.96
RB0602	0.1	5	417.1	450.8	471.5	516.1	99.0	1.60
		10	422.1	451.6	476.1	521.1	99.0	1.49
		15	424.1	456.2	481.4	530.1	106.0	1.45
		20	428.4	458.5	482.5	532.4	104.0	1.45
		25	428.9	461.7	485.3	535.5	106.6	1.39
		30	433.2	463.2	487.1	537.2	104.0	1.51
	4	5	423.2	445.2	465.2	501.9	78.7	2.49
		10	429.5	451.6	474.0	507.3	77.8	2.04
		15	435.8	455.8	478.1	507.6	71.8	2.53
		20	439.1	459.6	481.3	516.3	77.2	2.66
		25	447.3	462.1	484.5	517.5	70.2	2.65
		30	449.3	463.6	486.2	518.3	69.0	2.57
	7	5	430.7	452.9	466.2	489.2	58.5	2.76
		10	432.8	455.1	472.7	495.7	62.9	2.92
		15	435.7	458.3	478.5	502.7	67.0	2.84
		20	444.6	461.6	481.8	502.9	58.3	2.44
		25	447.8	467.4	484.2	508.2	60.4	2.77
		30	453.4	470.6	487.2	510.6	57.2	2.80

T_0 is the initial temperature point at which DSC curve deviates from the base line; T_e is the extrapolated onset temperature in DSC curve, T_p is the peak temperature and T_f is the finish temperature; ΔH_d is the decomposition heat. $\Delta T = T_f - T_0$

$f(\alpha)$ expression, and the values of E_a/(kJ mol^{-1}) and A/s^{-1} into Arrhenius equation (Eq. 1), the corresponding kinetic equations of the decomposition reaction of the propellants are obtained and shown in Table 4.

$$d\alpha/dt = Af(\alpha)e^{-E/RT} \quad (1)$$

From Table 4, one can find that high pressure can change the decomposition reaction mechanism function and kinetics of the propellants RB0601 and RB0602, and the effect on them is identical approximately with the increase in pressure. The control process of the main decomposition reaction obeys the rule of Avrami–Erofeev equation at high pressure instead of chemical reaction order model at normal pressure. High pressure makes the apparent activation energy decrease fast, and the decomposition reaction occurs easily. The mechanism functions are not changed by the ballistic modifier, the apparent activation energies are merely little changed, and the kinetic equations have a little difference between the two propellants.

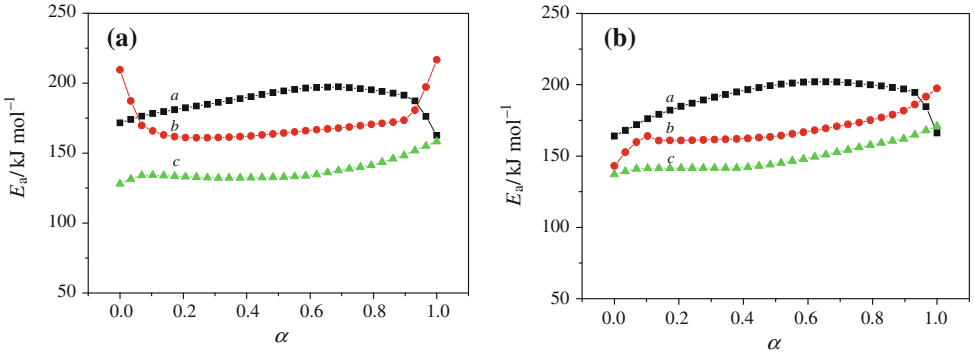

Fig. 2 E_a–α curves for the main exothermic decomposition process of propellants RB0601 (**a**) and RB0602 (**b**) Pressure (MPa): (*a*): 0.1; (*b*): 4; (*c*) 7

Table 2 Kinetic parameters for the main exothermic decomposition process of the propellants RB0601

Method	β	0.1 MPa			4 MPa			7 MPa		
		E_a	lg$A$	r	E_a	lg$A$	r	E_a	lg$A$	r
General integral	5	188.0	18.70	0.9983	151.0	14.64	0.9956	155.8	15.30	0.9966
	10	190.6	18.99	0.9970	161.6	15.91	0.9973	154.6	15.17	0.9986
	15	201.0	20.19	0.9965	147.1	14.21	0.9914	144.9	14.05	0.9998
	20	196.6	19.69	0.9969	161.3	15.86	0.9973	149.4	14.52	0.9990
	25	187.9	18.70	0.9950	163.0	16.03	0.9993	157.7	15.41	0.9989
	30	193.8	19.32	0.9955	163.4	16.09	0.9990	161.7	15.84	0.9988
Mac Callum–Tanner	5	188.8	18.74	0.9984	151.3	14.61	0.9961	155.9	15.25	0.9970
	10	191.4	19.05	0.9973	162.0	15.89	0.9976	154.9	15.14	0.9987
	15	201.9	20.27	0.9968	147.4	14.20	0.9923	145.2	14.01	0.9998
	20	197.8	19.77	0.9972	161.8	15.87	0.9976	149.8	14.51	0.9991
	25	188.9	18.77	0.9955	163.6	16.04	0.9993	158.2	15.41	0.9991
	30	194.8	19.41	0.9960	164.0	16.11	0.9991	162.3	15.84	0.9989
Šatava–Šesták	5	186.4	18.52	0.9984	151.0	14.62	0.9961	155.4	15.24	0.9970
	10	188.9	18.82	0.9973	161.1	15.84	0.9976	154.4	15.12	0.9987
	15	198.8	19.97	0.9968	147.4	14.24	0.9923	145.2	14.06	0.9998
	20	194.7	19.50	0.9972	161.0	15.81	0.9976	149.6	14.53	0.9991
	25	186.6	18.56	0.9955	162.6	15.98	0.9993	157.5	15.38	0.9991
	30	192.1	19.16	0.9959	163.0	16.04	0.9991	161.4	15.78	0.9989
Agrawal	5	188.0	18.70	0.9983	151.0	14.64	0.9956	155.8	15.30	0.9966
	10	190.6	18.99	0.9970	161.6	15.91	0.9973	154.6	15.17	0.9986
	15	201.0	20.19	0.9965	147.1	14.21	0.9914	144.9	14.05	0.9998
	20	196.6	19.69	0.9969	161.3	15.86	0.9973	149.4	14.52	0.9990
	25	187.9	18.70	0.9950	163.0	16.03	0.9993	157.7	15.41	0.9989
	30	193.8	19.32	0.9955	163.4	16.09	0.9990	161.7	15.84	0.9988
Mean		192.8	19.24		158.0	15.45		154.1	15.04	
Ozawa		192.5		0.9959	157.2		0.9973	152.5		0.9955
Kissinger		194.4	19.51	0.9955	157.4	15.49	0.9970	152.4	14.88	0.9950

The units of β, E_a, and lg$A$ are K min^{-1}, kJ mol^{-1}, and s^{-1}, respectively. The data obtained at 0.1 MPa are cited from Ref. 13. The same as in Table 3

Correlation between PDSC characteristic values and burning rates

On the combustion models for solid propellant, Miller et al. [19] thought that the burning rate (u) keeps a direct proportion to the decomposition rate on the surface of the solid propellant, and Brill et al. [20] obtained a formula composed of u^2, Arrhenius parameters for the condensed phase decomposition reaction, the decomposition heat, and the temperature on the burning surface. From the research

Table 3 Kinetic parameters for the main exothermic decomposition process of the propellants RB0602

Method	β	0.1 MPa			4 MPa			7 MPa		
		E_a	lg$A$	r	E_a	lg$A$	r	E_a	lg$A$	r
General integral	5	197.0	19.76	0.9997	145.2	14.01	0.9978	152.6	14.57	0.9964
	10	207.4	20.98	0.9999	152.8	14.88	0.9982	151.3	14.78	0.9986
	15	196.3	19.67	0.9991	157.1	15.40	0.9985	149.0	14.51	0.9986
	20	203.4	20.56	0.9988	150.1	14.64	0.9993	150.3	14.67	0.9989
	25	202.3	20.36	0.9987	158.2	15.52	0.9994	159.3	15.61	0.9993
	30	206.4	20.79	0.9991	154.8	15.15	0.9995	165.6	16.28	0.9991
Mac Callum–Tanner	5	197.7	19.81	0.9998	145.3	13.97	0.9980	152.7	14.83	0.9967
	10	208.4	21.06	0.9999	153.1	14.87	0.9984	151.5	14.75	0.9988
	15	197.3	19.74	0.9992	157.5	15.39	0.9986	149.2	14.49	0.9988
	20	204.5	20.64	0.9989	150.5	14.63	0.9993	150.6	14.65	0.9991
	25	203.3	20.45	0.9988	158.7	15.53	0.9995	159.8	15.61	0.9994
	30	207.6	20.89	0.9992	155.3	15.16	0.9994	166.2	16.30	0.9992
Šatava–Šesták	5	194.9	19.54	0.9998	145.4	14.02	0.9980	152.4	14.83	0.9967
	10	204.9	20.73	0.9999	152.8	14.86	0.9984	151.2	14.76	0.9988
	15	194.4	19.48	0.9992	156.9	15.36	0.9986	149.1	14.51	0.9988
	20	201.2	20.34	0.9989	150.3	14.65	0.9993	150.4	14.66	0.9991
	25	200.2	20.15	0.9988	158.0	15.49	0.9995	159.0	15.57	0.9994
	30	204.1	20.57	0.9992	154.8	15.15	0.9994	165.1	16.21	0.9992
Agrawal	5	197.0	19.76	0.9997	145.2	14.01	0.9978	152.6	14.57	0.9964
	10	207.4	20.98	0.9999	152.8	14.88	0.9982	151.3	14.78	0.9986
	15	196.3	19.67	0.9991	157.1	15.40	0.9985	149.0	14.51	0.9986
	20	203.4	20.56	0.9988	150.1	14.64	0.9993	150.3	14.67	0.9989
	25	202.3	20.36	0.9987	158.2	15.52	0.9994	159.3	15.61	0.9993
	30	206.4	20.79	0.9991	154.8	15.15	0.9995	165.6	16.28	0.9991
Mean		201.8	20.32		153.1	14.93		154.7	15.08	
Ozawa		204.0		0.9934	152.8		0.9989	152.2		0.9976
Kissinger		206.5	20.88	0.9929	152.8	15.00	0.9988	152.1	14.91	0.9974

results, one can know that the burning rate keeps a direct proportion to the square root of the reaction rate constant $k = A\exp(-E/RT)$ and that of the work pressure. On the basis of the preceding works, Liu et al. [21] correlated the characteristic values of PDSC and the burning rates by a liner empirical formula:

$$u = k_u (p\,\Delta H_d/\Delta T)^{1/2} + C \tag{8}$$

where u is the burning rate of the propellant in mm s^{-1}; k_u is the correlation factor of the burning rate with PDSC characteristic value in mm $(g\ K)^{1/2}\ s^{-1}$ $(MPa\ J)^{-1/2}$; p is the work pressure in MPa; $\Delta H_d$is the decomposition heat in J g^{-1}; $\Delta T = T_f - T_0$; C is a constant.

As the heating rate of PDSC is controlled by computer program and keeping 10 K min^{-1} during the whole experiment, thus, ΔT is corresponding to the decomposition reaction time (Δt), and $\Delta H_d/\Delta T$ can be thought as the rate of the heat release or decomposition rate on condition that the decomposition heat keeps a direct proportion to the conversion degree (α). Moreover, the pressure (p) is an important factor, which affected the burning rate and decomposition reaction, and be introduced into the empirical formula (8). As a matter of fact, the formula integrates the two important factors, which affected the burning rate: the decomposition rate and the pressure.

The PDSC characteristic values and burning rates for the propellants RB0601 and RB0602 are shown in Table 5. The u versus $(p\,\Delta H_d/\Delta T)^{1/2}$ curves were drawn and the slope coefficients (k_u), the constants (C) and the linear correlation coefficient (r) were obtained by linear regression and shown in Eqs. 9 and 10.

$$\text{RB0601}: u = 0.833\,(p\,\Delta H_d/\Delta T)^{1/2} - 1.65 \quad r = 1 \tag{9}$$

$$\text{RB0602}: u = 0.924\,(p\,\Delta H_d/\Delta T)^{1/2} + 0.06 \quad r = 0.9902 \tag{10}$$

The results show the good linear relation of u and $(p\,\Delta H_d/\Delta T)^{1/2}$and the good fittings of the formula for the

Table 4 Mechanism functions, apparent activation energies, and kinetic equations for the propellants RB0601 and RB0602

Sample	P/ MPa	Section selected	Mechanism and mechanism function	Mechanism function number	E_a/ kJ mol^{-1}	Kinetic equation
RB0601	0.1	$0.08 \leq \alpha \leq 0.98$	Reaction order model, $G(\alpha) = (1-\alpha)^{-1} - 1$, $f(\alpha) = (1-\alpha)^2$	37	192.8	$d\alpha/dt = 10^{19.24}(1-\alpha)^2 e^{-2.32\times10^4/T}$ (2)
	4	$0.08 \leq \alpha \leq 0.90$	Avrami–Erofeev equation, assumes random nucleation and its subsequent growth, $n = 3/4$ $G(\alpha) = [-\ln(1-\alpha)]^{3/4}$, $f(\alpha) = (4/3)(1-\alpha)[1-(1-\alpha)]^{1/4}$	15	158.0	$d\alpha/dt = 10^{15.57}(1-\alpha)[1-(1-\alpha)]^{1/4} e^{-1.90\times10^4/T}$ (3)
	7	$0.02 \leq \alpha \leq 0.80$	Avrami–Erofeev equation, assumes random nucleation and its subsequent growth, $n = 2/3$, $G(\alpha) = [-\ln(1-\alpha)]^{2/3}$, $f(\alpha) = (3/2)(1-\alpha)[1-(1-\alpha)]^{1/3}$	14	154.1	$d\alpha/dt = 10^{15.21}(1-\alpha)[1-(1-\alpha)]^{1/3} e^{-1.85\times10^4/T}$ (4)
RB0602	0.1	$0.20 \leq \alpha \leq 0.96$	Reaction order model, $G(\alpha) = (1-\alpha)^{-1} - 1$, $f(\alpha) = (1-\alpha)^2$	37	201.8	$d\alpha/dt = 10^{20.32}(1-\alpha)^2 e^{-2.43\times10^4/T}$ (5)
	4	$0.10 \leq \alpha \leq 0.80$	Avrami–Erofeev equation, assumes random nucleation and its subsequent growth, $n = 3/4$ $G(\alpha) = [-\ln(1-\alpha)]^{3/4}$, $f(\alpha) = (4/3)(1-\alpha)[1-(1-\alpha)]^{1/4}$	15	153.1	$d\alpha/dt = 10^{15.05}(1-\alpha)[1-(1-\alpha)]^{1/4} e^{-1.84\times10^4/T}$ (6)
	7	$0.02 \leq \alpha \leq 0.80$	Avrami–Erofeev equation, assumes random nucleation and its subsequent growth, $n = 2/3$, $G(\alpha) = [-\ln(1-\alpha)]^{2/3}$, $f(\alpha) = (3/2)(1-\alpha)[1-(1-\alpha)]^{1/3}$	14	154.7	$d\alpha/dt = 10^{15.25}(1-\alpha)[1-(1-\alpha)]^{1/3} e^{-1.86\times10^4/T}$ (7)

The mechanism function numbers are cited from Refs. 14 and 15

Table 5 The PDSC characteristic values and burning rates for the propellants RB0601 and RB0602

Sample	P/MPa	T_0/K	T_p/K	T_f/K	ΔT/K	ΔH_d/ J g^{-1}	$(p\Delta H_d/\Delta T)^{1/2}$/ (MPa J g^{-1} K^{-1})$^{1/2}$	u/mm s^{-1}
RB0601	0.1	426.2	476.9	530.5	104.3	1.45×10^3	1.18	–
	2	430.3	473.8	505.3	74.9	2.14×10^3	7.56	4.66
	4	430.8	473.7	502.2	71.4	2.63×10^3	12.1	8.41
	6	435.3	473.4	499.8	64.5	2.70×10^3	15.8	11.52
	7	428.1	475.8	497.9	69.8	3.10×10^3	17.6	13.02
RB0602	0.1	422.1	476.1	521.1	99.0	1.49×10^3	1.23	–
	2	427.0	473.4	505.8	78.8	2.00×10^3	7.12	6.24
	4	429.5	474.0	507.3	77.8	2.04×10^3	10.2	9.88
	6	437.4	473.6	502.0	64.6	2.34×10^3	14.7	14.01
	7	432.8	472.7	495.7	62.9	2.92×10^3	18.0	16.32

The burning rate data are cited from Ref. 13

propellants in pressure range (2–7 MPa) of PDSC. It is found that k_u keeps a similar changing trend with u, and can be used to study the effect of the ballistic modifier or the other component on the burning rates.

Conclusions

The high-pressure thermal properties and their correlation with burning rates of the BTATz-CMDB propellants were investigated using PDSC. High pressure restrains the volatilization of NG, accelerates the decomposition reaction, and makes the reaction occur easily. High pressure can change the decomposition reaction mechanism function and kinetics, and the control process of the main exothermal decomposition reaction obeys the rule of Avrami–Erofeev equation at high pressure and chemical reaction at normal pressure. The decomposition reaction mechanism function can not be changed by the ballistic modifier. The correlation between PDSC characteristic values and burning rates was carried out and found that u and$(p\,\Delta H_d/\Delta T)^{1/2}$keep a good linear relation, k_u keeps a similar changing trend with u, and it can be used to study the effect of the ballistic modifier or the other component on the burning rates.

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