

# EFFECT OF AMMONIUM OXALATE/STRONTIUM CARBONATE ON THE BURNING RATE CHARACTERISTICS OF COMPOSITE PROPELLANTS

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AP/HTPB based composite propellants with additives such as ammonium oxalate (AO), mixture of ammonium oxalate and strontium carbonate (SC) was investigated by burning rate, TG-DTG and FTIR experiments. The results show that the burning rates of these propellants are decreased significantly. TG-DTG experiments indicate that decomposition temperatures of AP with these additives are increased. Furthermore, the activation energy of the decomposition reaction of AP is also increased in the presence of AO or AO/SC. These results show that AO or AO/SC restrains the decomposition of AP. The burning rates of these propellants are decreased. The burning rate temperature sensitivity of AP/HTPB based propellants is reduced significantly by the addition of AO or AO/SC. But the effect of AO is less than that of AO/SC. AO/SC is better effect to reduce temperature sensitivity and at the same time, to reduce pressure exponent. The reduced heat release at the burning surface of AP/HTPB/AO is responsible for the reduced temperature sensitivity. Synergetic action is probably produced between AO and SC within AP/HTPB based propellants in the pressure range tested. This synergetic effect causes the heat release to reduce and the burning surface temperature to increase. Moreover, it makes the net exothermal reaction of condensed phase become little dependent on  $T_0$ . Thus, the burning rate temperature sensitivity is reduced.

**Keywords:** burning rate characteristic, composite propellants, TG-DTG

## Introduction

Solid rockets/missiles are associated closely with the burning rate temperature sensitivity of propellants. To the same motors and their projectile filling at different temperatures, if temperature sensitivity is very large, the motors will consume a number of fuels, accuracy of release fire will be bad and safety performance of release fire will be lack of guarantee [1]. For rockets/missiles, obviously, temperature sensitivity should be as low as possible so that the pressure and the thrust are least affected by operation over a broad range of temperatures.

The burning rate ( $r$ ) of solid propellant is known to be depended on the initial propellant temperature ( $T_0$ ). The variation of  $r$  with  $T_0$  at constant pressure ( $p$ ) is defined as the burning rate temperature sensitivity ( $\sigma_p$ ) and is displayed as [2]:

$$\sigma_p = \frac{1}{r} \left[ \frac{\partial r}{\partial T_0} \right]_p = \left[ \frac{\partial \ln r}{\partial T_0} \right]_p \quad (1)$$

As usual, variable trend of temperature sensitivity and pressure exponent is consensus. But experience shows pressure exponent changes remarkably with pressure and temperature sensitivity changes appreciably with initial temperature.

The burning rate temperature sensitivity is determined by many factors such as initial temperature, pressure, particle size and additive addition, etc. The influence of initial temperature on burning rate is reported as follows [3]: (a) When initial temperature changes, absorbing heat of propellants also changes, so this causes a change in net heat release of condensed phase and burning rate changes. (b) When initial temperature decreases, the final flame temperature also decreases and the heat flux reduces from gas phase to burning surface, so burning rate decreases. (c) When the initial temperature decreases, the percentage of AP decomposition increases by means of endothermic reaction, so the burning rate decreases. (d) When initial temperature decreases, oxidizer particles which are heated at short time melt difficultly. This reduces the fraction of AP that decomposes in the subsurface and the fraction of AP that reacts with binder and makes heat release of condensed phase reaction decrease, so the burning rate reduces. Kubota [4] studied the effects of burning rate temperature sensitivity on AP particle size and catalyst. Experiment result indicates that the temperature sensitivity decreases with the AP particle size becoming fine. The burning rate temperature sensitivity also decreases by the addition of BEFP [2,2-bis(ethylferrocenyl) propane] in AP. But it is evi-

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dent that the temperature sensitivity is decreased more effectively by the addition of BEFP than by the addition of fine AP particles. Kulkarni [5] studied the temperature sensitivity in AP propellants with iron oxide. The experiment data indicates that iron oxide can enhance burning rate and reduce temperature sensitivity simultaneously. Atwood [6] investigated the effect of pressure on burning rate temperature sensitivity of AP, HMX, ADN, RDX, CL-20 and HNF and found, in general, as the experimental pressure is increased, the burning rate temperature sensitivity decreases. This is most apparent in the CL-20. AP is the only exception to this observation. He also found that at pressure below 4 MPa, RDX had the lowest value of temperature sensitivity.

The objective of this investigation is to find appropriate additives in order to reduce the temperature sensitivity. The propellants with various additives can decrease the environment effect on propellants performance and can be used over a wide range of temperature.

## Experimental

### *Burning rate measurement*

The propellant samples (N-0–N-2) tested in this study consist of AP particles with HTPB (hydroxy-terminated polybutadiene) as a binder and Al powder (average particle size 33  $\mu\text{m}$ ). Their main compositions of the propellants are shown in Table 1. The measurements of burning rate were performed with a strand burner set in a temperature conditioner operated in a range of temperature from  $-40$  to  $50^\circ\text{C}$ . The temperature of the nitrogen was also conditioned by a heat exchanger set in the temperature conditioner.

### *TG-DTG studies of additives on AP*

In order to understand the effects of additives on AP, non-isothermal TG-DTG analyses of AP and AP containing AO, SC, AO/SC as additives were done with a DT-50 (Shimadzu) TG instrument at a heating rate of  $10^\circ\text{C min}^{-1}$  (at atmosphere=flowing  $\text{N}_2$  gas at a

rate of  $20 \text{ mL min}^{-1}$ ). The chemical compositions of thermal analyses (M-0–M-3) are shown in Table 1. Since the oxidation reaction temperature of Al is much higher than the decomposition temperature of AP, the reaction of Al powder with additives is not considered. It was reported that [7] the additives had no effects on the decomposition of HTPB, so HTPB was not added to the thermal analyses sample.

### *In situ FTIR experiments*

The IR spectra of M-2 were recorded using KBr pellets on a Perkin by Nicolet FTIR spectrometer MAGNA-IR 750 in the temperature range of  $237$ – $450^\circ\text{C}$ . Spectra over a range of  $4000$  to  $400 \text{ cm}^{-1}$  with a resolution of  $2 \text{ cm}^{-1}$ . The heating rate is  $2^\circ\text{C min}^{-1}$  (at atmosphere= $\text{N}_2$  gas). For temperature-controlled FTIR spectra the samples were prepared in KBr pellets using a heating device and the thermocouple contacts the sample. The FTIR analysis was performed on the solid residue of the sample during the thermal decomposition.

## Results and discussion

### *The effects of additives on the burning characteristics of AP/HTPB based propellants*

The burning rates of propellant N-0 are shown in Table 2. The reducing percentages of burning rates of propellants N-1 and N-2 compared with propellant N-0 are presented in Table 3 at constant initial temperature. As shown in Table 3 the reducing percentages of burning rates of propellant N-1 and N-2 become larger and larger with increasing pressure. Although the effect of AO as the additive on the burning rate is evident when pressure increases, the percentage of reducing the burning rate is limit. When the pressure is below about 5 MPa, AO acts more effectively on the burning rate of propellant N-1. However, when the pressure is more than about 5 MPa, the reducing percentage of burning rate of AO as the additive within propellant N-1 is much smaller than AO/SC as the additive within propellant N-2. In the case of pressure exponent, the additive of AO or AO/SC in AP/HTPB based propellants decreases the pressure exponent; especially the effect of AO/SC on reducing the pressure exponent is more efficient than that of AO. It should be noted that the pressure exponent of propellant N-2 is lower 61.99% than that of propellant N-0. It is thought that the pressure exponent is decreased due to the reducing percentage of burning rate at high pressure that is larger than that at low pressure, where the effect of AO/SC is considerably evident.

**Table 1** Propellant main compositions and thermal analysis compositions

Sample	Compositions	Mass ratio
N-0	HTPB/AP/Al	10:66:17
N-1	(HTPB+AP+Al)/AO	93:4
N-2	(HTPB+AP+Al)/SC/AO	93:3:1
M-0	AP/Al	66:17
M-1	(AP+Al)/AO	83:4
M-2	(AP+Al)/SC	83:4
M-3	(AP+Al)/SC/AO	83:3:1

**Table 2** The burning rates and pressure exponent for propellant N-0 at different N<sub>2</sub> pressure at 20°C

Sample	Burning rate/mm s <sup>-1</sup>					Pressure exponent
	3 MPa	4 MPa	5 MPa	6 MPa	7 MPa	
N-0	4.46	4.91	5.36	5.69	6.25	0.4086

**Table 3** The reducing percentages of burning rates and pressure exponents for propellants N-1 and N-2 at different N<sub>2</sub> pressure compared with propellant N-0 at 20°C

Sample	Reducing burning rate/%					Reducing pressure exponent/%
	3 MPa	4 MPa	5 MPa	6 MPa	7 MPa	
N-1	13.2	17.52	22.01	21.79	24.48	38.69
N-2	9.87	16.50	21.83	23.20	29.12	61.99

The burning rates of propellant N-0 are shown in Table 4. The reducing percentages of burning rates of propellants N-1 and N-2 compared with propellant N-0 at constant pressure 6.18 MPa are shown in Table 5. It is seen from Table 5 that the reducing percentage of burning rate is smaller at lower temperature, but it increases with increasing initial temperature. There is an exception at about 0°C. At more than 0°C, the reducing percentage of burning rate of AO/SC is larger than that of AO. The higher the initial temperature is, the larger the reducing percentage of burning rate of AO/SC is. It is evident that the addition of AO or AO/SC in AP/HTPB based propellants also reduces burning rate temperature sensitivity. In comparison of the two additives, AO/SC is the better additive and decreases the temperature sensitivity of AP/HTPB based propellants almost 1 time. From above facts it can be concluded that AO or AO/SC within AP/HTPB based propellants not only decreases the pressure exponent, but also decreases the temperature sensitivity, especially the latter.

#### *Analysis on reducing the burning rates of AP/HTPB based propellants with additives*

TG-DTG experiments were carried out in order to understand the effect of AO or AO/SC on the inhibition of the burning rate of AP/HTPB based propellants. The curves of DTG curves and FT-IR are shown in Figs 1 and 2.

The thermolysis of sample M-0 includes two steps (Fig. 1). The first step which peak temperature is 291°C corresponds to the low-temperature decomposition (LTD) of AP. The second step which peak temperature is 372.4°C corresponds to the high-temperature decomposition (HTD).

The sample of M-1 shows a three-stage decomposition (Fig. 1). The first stage is not quietly obvious. The peak temperature for LTD of AP is 294.5°C and the peak temperature for HTD of AP is 382.5°C. Both the peak temperatures are higher than those of sample M-0. This indicates that AO has a good inhibition effect on the decomposition of AP and consequently leads to reduce the burning rate of AP/HTPB based propellants. Figure 1 also shows the peak temperature of 198.2°C which should be associated with the peak temperature of AO decomposition in sample M-1, because it is an easy decomposition substance. NH<sub>3</sub>, H<sub>2</sub>O, CO<sub>2</sub> and CO are produced by the decomposition of (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> [8]. The thermal decomposition of AP at low temperature has been reported in detail previously [9].

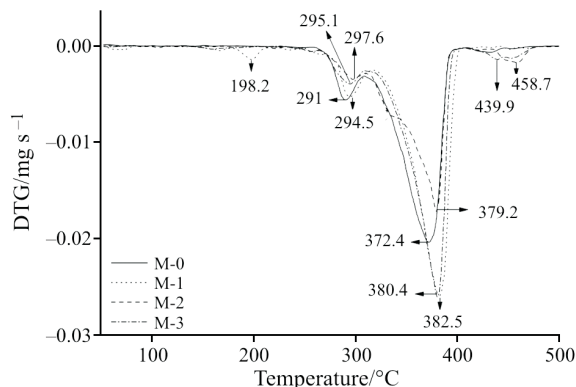
Since the decomposition temperature of AO is lower, the decomposition product of AO shifts the chemical balance of decomposition of AP to left, so that the decomposition reaction of AP is inhibited. According to the change in Gibbs free energy of the system  $\Delta G = \Delta H - T\Delta S$ , if the reaction is spontaneous, it must be  $\Delta G < 0$ . For some substances, although both

**Table 4** The burning rates and temperature sensitivity for propellant N-0 at different initial temperature at 6.18 MPa

Sample	Burning rate/mm s <sup>-1</sup>					Temperature sensitivity
	50°C	20°C	0°C	-20°C	-40°C	
N-0	5.83	5.42	5.15	5.06	4.28	0.0021

**Table 5** The reducing percentages of burning rate and temperature sensitivities for propellants N-1 and N-2 at different initial temperature compared with propellant N-0 at 6.18 MPa

Sample	Reducing burning rate/%					Reducing temperature sensitivity/%
	50°C	20°C	0°C	-20°C	-40°C	
N-1	14.58	13.47	11.65	12.45	10.46	23.81
N-2	16.47	14.21	11.47	11.66	8.16	47.62



**Fig. 1** DTG curves of samples M-0–M-3 at a heating rate of  $10^{\circ}\text{C min}^{-1}$  and a flowing rate of  $\text{N}_2$  gas of  $20 \text{ mL min}^{-1}$

$\Delta H$  and  $\Delta S$  change with temperature,  $\Delta H$  changes a little with temperature. On the other hand,  $\Delta S$  is less than  $\Delta H$ . Thus, with increasing of the decomposition temperature, the  $-T\Delta S$  term becomes relatively more important in determining the sign and magnitude of  $\Delta G$ . It is the reason that the peak temperature for LTD of AP is raised as shown in Fig. 1.

The HTD of AP belongs to gas phase reaction. It is known that the thermolysis of AO is highly endothermic [7]. The decomposition products of AO such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  enable the concentration of  $\text{HClO}_4$  to become dilute and carry away the heat from the gas phase, thus the peak temperature for HTD of AP is also raised.

From above-mentioned results, it can be seen that the concentrations of gas such as  $\text{NH}_3$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  which inhibit the decomposition of AP with increasing the pressure. Consequently, the decomposition reactions of AP and  $\text{HClO}_4$  take place more difficultly at high pressure than at low pressure, i.e., the effect of reducing the burning rate become more and more evident with the pressure increasing.

It can be presented from Fig. 1 that the peak temperature of AP decomposition within M-2 is higher than that of M-0. Both the peak temperatures for LTD and HTD of AP are increased by 6.6 and  $6.8^{\circ}\text{C}$  in the presence of SC respectively. The addition of SC in AP increases temperatures for LTD and HTD of AP, so as to reduce its propellant burning rate. SC is a substance that has a high decomposition temperature. The thermal analysis of pure SC shows that the initial mass loss takes place at  $745^{\circ}\text{C}$  and the peak temperature is about  $761.5^{\circ}\text{C}$ . But Fig. 1 shows the last peak temperature is only  $458.7^{\circ}\text{C}$ , so it is evaluated that the reaction of SC was given below:

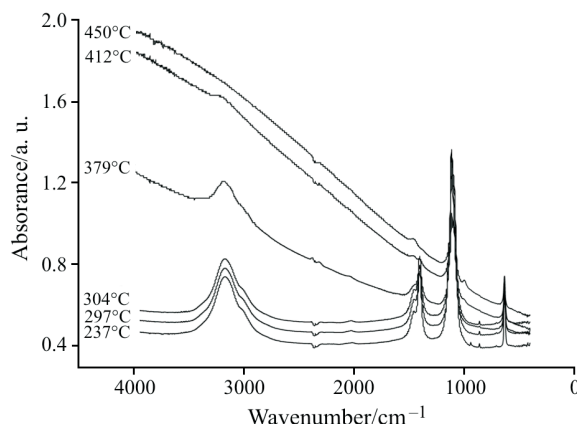
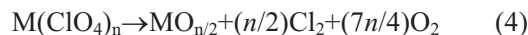
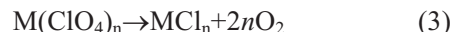


$458.7^{\circ}\text{C}$  should be peak temperature of  $\text{Sr}(\text{ClO}_4)_2$  decomposition.

FTIR techniques have been widely used today to characterize materials [10, 11]. It is a technique which provides data for a comprehensive understanding of

decomposition processes. In order to certify the generation of  $\text{Sr}(\text{ClO}_4)_2$ , the FTIR experiments were carried out. Figure 2 shows typical FTIR spectrums of the solid residues obtained from the thermal decomposition of sample M-2 at different temperatures in our study. At  $237^{\circ}\text{C}$ , the bands at  $628.08 \text{ cm}^{-1}$ , and in the range of  $1090\text{--}1141 \text{ cm}^{-1}$  are the characteristic absorption peaks of  $\text{ClO}_4^-$ . The  $\text{CO}_3^{2-}$  bands showed a strong peak at  $1455.50 \text{ cm}^{-1}$  and a weak peak at  $859.38 \text{ cm}^{-1}$ . The band at  $1393.44 \text{ cm}^{-1}$  is assigned to the vibrations of  $\text{NH}_4^+$  and the other band at  $3168.62 \text{ cm}^{-1}$  is attributed to the N–H vibrations of the  $\text{NH}_4^+$ . Increasing the temperature to  $297^{\circ}\text{C}$ , the bands of  $1091$  and  $1141 \text{ cm}^{-1}$  disappear. The bands at  $304^{\circ}\text{C}$  almost match together that at  $297^{\circ}\text{C}$ . On the other hand, the intensity of the bands associated with  $\text{CO}_3^{2-}$ ,  $\text{NH}_4^+$  and N–H changes little. However, heating to  $379^{\circ}\text{C}$  resulted in important changes in the spectra. All of intensity of the bands is apparently weakened. Especially, the intensity of the absorption band found at  $1455 \text{ cm}^{-1}$  almost completely disappears. These imply that the amounts of different groups reduce. Heating to  $412^{\circ}\text{C}$  leads to the complete disappearance of the absorption bands of  $\text{CO}_3^{2-}$ , and the absorption bands of  $\text{NH}_4^+$  and N–H also basically disappear, but the absorption bands of  $\text{ClO}_4^-$  still exist. Heating to  $450^{\circ}\text{C}$ , there are only the absorption bands of  $\text{ClO}_4^-$ . Although the absorption band of  $\text{NH}_4^+$  disappears, the absorption bands of  $\text{ClO}_4^-$  still exist. This indicates that  $\text{Sr}(\text{ClO}_4)_2$  has formed. Thus it can be certified in Fig. 1 that  $458.7^{\circ}\text{C}$  is the peak temperature of  $\text{Sr}(\text{ClO}_4)_2$  decomposition.

Metal perchlorates are decomposed to metal oxides or metal chlorides due to the characteristics of positive ion. When the temperature is less than  $600^{\circ}\text{C}$ , reactions are spontaneous in measurable rate [12].

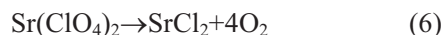


**Fig. 2** In situ FTIR spectra of sample M-2 at 237, 297, 304, 379, 412 and  $450^{\circ}\text{C}$

which reaction is spontaneous in Eqs (3) and (4) according to Gibbs free energy of products. From the manual of thermodynamic data, Gibbs free energy of Ca, Sr, Ba chlorides are gained:  $-826.9$ ,  $-864.20$ ,  $-896.26$   $\text{kJ mol}^{-1}$ . Gibbs free energy of Ca, Sr, Ba oxides are  $-646.15$ ,  $-608.37$  and  $574.50$   $\text{kJ mol}^{-1}$ , respectively. Ca, Sr, Ba perchlorates prefer to decompose to metal chlorides, because of free energy of these products,

$$\Delta G_f^0(\text{chloride}) - \frac{1}{2} \Delta G_f^0(\text{oxide}) < 0 \text{ kJ mol}^{-1} \quad (5)$$

Therefore it indicates the decomposition of  $\text{Sr}(\text{ClO}_4)_2$  will proceed as follows:



It can be seen that  $\text{Sr}(\text{ClO}_4)_2$  is more stable than that of  $\text{HClO}_4$  because the peak temperature of  $\text{Sr}(\text{ClO}_4)_2$  decomposition is  $458.7^\circ\text{C}$  (Fig. 1), but the peak temperature of  $\text{HClO}_4$  decomposition is  $372.4^\circ\text{C}$  (Fig. 1). As a result, the temperature for HTD of AP is increased by incorporation of SC.

The product  $\text{SrCl}_2$  decomposes difficultly, which covers on the burning surface and inhibits the decomposition of AP in the condensed phase. Thus the temperature for LTD of AP is increased. In a sense, the mechanism of inhibiting decomposition of AP is the similar to  $\text{CaCl}_2$  and  $\text{SrCl}_2$  [13]. At the low pressure, product  $\text{CO}_2$  diffuses easily from the burning surface to gas phase, so the effect of physical covering on the burning surface is small. However,  $\text{CO}_2$  diffuses difficultly with increasing the pressure and accumulates at the burning surface. At the same time, the reaction rate changes drastically and the concentration of  $\text{SrCl}_2$  at the burning surface changes larger, consequently, the synergetic effects of these two aspects inhibit the decomposition of AP. Thus the effect on the reducing burning rate at high pressure is much better than that at low pressure.

The DTG curve of sample M-3 is shown in Fig. 1. It can be seen that the decomposition peak of AO disappears. This may coincide with the LTD of AP. The two peak temperatures of AP decomposition are  $295.1$  and  $380.4^\circ\text{C}$ , respectively. The addition of AO/SC increases the LTD and HTD of AP by  $4.1$  and  $8.0^\circ\text{C}$  compared with M-0. It is evident that SC and AO did not produce synergetic effects at low pressure. It can be caused that CO produced by AO decomposition reacts with  $\text{O}_2$  produced by  $\text{HClO}_4$  decomposition. Reaction CO with  $\text{O}_2$  catalyzes the decomposition of  $\text{Sr}(\text{ClO}_4)_2$  and reduces the inhibition to the decomposition of AP. But at the high pressure, AP particles are trapped into the burning surface and decompose difficultly. At the same time,  $\text{CO}_2$  strongly covers on the burning surface and thus

inhibits proceeding of the reaction. Furthermore, AO and SC are rather inhibitors for the burning rate of AP/HTPB based propellants at the high pressure and produce synergetic effects, so that they lead to reduce the burning rate significantly.

Kulkarni *et al.* [5] and Miyata *et al.* [14] reported that the burning rate of AP/HTPB propellant with SC as an additive decreased because of an increase in the onset temperature of gasification reaction by the addition of SC, similarly, there is an increase in the surface decomposition temperature on incorporation of the additive. This is the same as the results that the decomposition temperature of AP is increased on incorporation of the additives such as AO and AO/SC.

In order to study the effect of the activation energy on the decomposition reaction of AP, the activation energy  $E_a$ , pre-exponential factor  $A$  and rate constant  $k$  shown in Table 6 are calculated by using the Kissinger method [15, 16] in this paper. The heating rates  $5$ ,  $10$ ,  $20$  and  $30^\circ\text{C min}^{-1}$  were used in TG-DTG experiments at  $0.1$  MPa. From the results listed in Table 6 the additives of AO, SC and AO/SC increased the activation energy of the HTD of AP by  $63.09$ ,  $62.01$  and  $50.25$   $\text{kJ mol}^{-1}$ , respectively. It is indicated that they can easily inhibit the thermal decomposition of AP, so they decrease the burning rate of their propellants.

**Table 6** Calculated values of the kinetic parameters for the decomposition reaction of AP with additives in flowing  $\text{N}_2$  determined from TG-DTG curves at various heating rate

Sample	$E_a/\text{kJ mol}^{-1}$	$\lg A/\text{s}^{-1}$	$K/\text{s}^{-1}$
M-0	98.98	7.55	0.4142
M-1	162.07	12.66	0.4767
M-2	160.99	12.73	0.6852
M-3	149.23	11.63	0.4781

#### Analysis on reducing the burning rate temperature sensitivity with additives

According to the temperature sensitivity equation is derived [17]:

$$\sigma_p = \left( \frac{\partial \ln \phi}{\partial T_0} \right)_p - \left( \frac{\partial \ln \psi}{\partial T_0} \right)_p = \phi + \psi \quad (7)$$

and

$$\psi = T_s - T_0 - Q_s / C_p \quad (8)$$

Substituting Eq. (8) into  $\psi = -(\partial \ln \psi / \partial T_0)_p$ , one can get

$$\psi = - \left( \frac{\partial \ln \psi}{\partial T_0} \right)_p = \frac{1 - (\partial T_s / \partial T_0)_p}{T_s - T_0 - Q_s / C_p} \quad (9)$$

where  $\phi$  is the temperature sensitivity of the gas phase reaction,  $\psi$  is the temperature sensitivity of the condensed phase reaction.

Most studies have suggested that the ballistic modifier is active mainly in the condensed phase [18–20]. Therefore, the temperature sensitivity of condensed phase reaction plays more dominant role in  $\sigma_p$  than that of the gas phase reaction. The temperature sensitivity of gas phase reaction is relatively independent of the physico-chemical properties of the chemical ingredients mixed within the propellant, thus it has less effect on  $\sigma_p$ . Based on Eq. (9) it is shown that  $Q_s$ ,  $T_s$  and  $(\partial T_s/\partial T_0)_p$  play dominant roles on the determination of  $\psi$ .

Above-mentioned facts show that the decomposition product of AO shifts the chemical balance of the decomposition of AP and inhibits the decomposition of AP. Therefore, it causes the heat release to reduce at the burning surface. According to Eq. (9),  $\psi$  decreases as the burning surface heat release  $Q_s$  decreases. Consequently, the addition of AO within AP/HTPB based propellants decreases the heat release at the burning surface and the temperature sensitivity of the condensed phase reaction  $\psi$  decreases. Thus, the burning rate temperature sensitivity  $\sigma_p$  of AP/HTPB based propellants decreases. It can be seen that the reduced  $\sigma_p$  of AP/HTPB/AO is caused by the decreased heat release at the burning surface.

On the basis of the decomposition of sample M-2, it is known that  $\text{Sr}(\text{ClO}_4)_2$  is more stable than  $\text{HClO}_4$ , so that it can accumulate transiently at the burning surface. This can be testified by FTIR. Thus, it may inhibit mass transfer of AP from the condensed phase to the gas phase and reduce heat transfer from the gas phase to the condensed phase. Therefore, this leads to the net exothermal reaction of condensed phase becoming little dependent on  $T_0$ . Since the burning rate is determined by the heat transferred back from the gas phase to the burning surface and the heat generated at the burning surface. The heat release  $Q_s$  is little dependent on  $T_0$ , i.e., the burning rate is little dependent on  $T_0$ , so  $\sigma_p$  decreases. At the same time, the decomposition product  $\text{SrCl}_2$  of  $\text{Sr}(\text{ClO}_4)_2$  covering on the burning surface has the function of accumulation of heat. This can make the burning surface temperature increase. The presumption can be proved by the review [21], which reported that the addition of SC within AP/HTPB increased the surface temperature from 430 to 700°C. From Eq. (9), it can be seen that the  $\psi$  decreases as the burning surface temperature increases.

The addition of AO/SC within AP/HTPB propellant decreases the temperature sensitivity probably due to the synergetic effect of AO and SC,

i.e., AO/SC may reduce the heat release at the burning surface and increase the burning surface temperature. Furthermore, AO/SC may cause the net exothermal reaction of condensed phase to become little dependent on  $T_0$ . However, these points need more experimental evaluations and thus further studies are required. But the results reported in this study show the overall combustion mechanisms of AO and AO/SC with AP/HTPB based propellants.

## Conclusions

Based on this study, the addition of AO or AO/SC within AP/HTPB based propellants reduces the burning rate due to increase both the decomposition temperature of AP and the activation energy of AP decomposition reaction. The effect of AO/SC is greater than that of AO at high pressure. At the same time, the pressure exponent of AP/HTPB is reduced significantly by the addition of AO or AO/SC due to the reducing in burning rate at high pressure that is larger than that at low pressure.

The burning rate temperature sensitivity of AP/HTPB based propellants is also decreased by the addition of AO or AO/SC. The burning rate temperature sensitivity of condensed phase reaction plays a dominant role in  $\sigma_p$ . Since the heat release at the burning surface decreases,  $\psi$  of AP/HTPB/AO is reduced. Thus  $\sigma_p$  is reduced. AO and SC may generate synergetic effects within AP/HTPB based propellants and make the heat release at the burning surface reduce. Furthermore, AO/SC may increase the burning surface temperature. These would all tend to decrease  $\psi$ , and then decrease  $\sigma_p$ . In addition, AO/SC may cause the net exothermal reaction of condensed phase to become little dependent on  $T_0$  and decrease  $\sigma_p$ .

## Nomenclature

AP	ammonium perchlorate
TG	thermogravimetry
DTG	derivative thermogravimetry
FTIR	Fourier transform infrared spectroscopy
HTPB	hydroxy-terminated polybutadiene
AO	ammonium oxalate
SC	strontium carbonate
$\sigma_p$	burning rate temperature sensitivity
HTD	the high-temperature decomposition
LTD	the low-temperature decomposition
HMX	cyclotetramethylene tetranitrimine
ADN	ammonium dinitramide
RDX	cyclotrimethylenetrinitramine
CL-20	hexanitrohexaazaisowurtzitane
HNF	hydrazinium nitroformate

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