

文章编号: 1000-8055(2012)05-1179-06

Particle size effect on ammonium perchlorate decomposition kinetics

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Abstract: The decomposition kinetic parameters of ammonium perchlorate (AP) having different grain size ($10-390\mu\text{m}$) were investigated through simultaneous DSC/TGA (differential scanning calorimetry/thermal gravimetric analysis) analyzer in a dynamic nitrogen atmosphere under heating rate of 40K/min . The kinetic parameters such as activation energy and pre-exponential factor were determined by the modified isoconversional method. The Brzdzauer-Emmett-Teller (BET)-method was applied to measure AP specific surface areas. The results show that the higher the AP particle size the lower the determined kinetic parameters and are matched with some important literatures.

Key words: ammonium perchlorate; particle size; specific surface area; thermal decomposition; thermogravimetry

CLC number: V435

Document code: A

Introduction

Oxidizer and polymeric binder are the major ingredients of the composite solid propellant formulations. Oxidizer decomposition plays a significant role during the propellant combustion^[1]. Since ammonium perchlorate (AP) was used as a main oxidizer in composite solid propellants technology, its thermal decomposition has been studied more frequently than that of any other oxidizer. It has been found that AP thermal decomposition is rather complex and exhibits several unusual characteristics^[2-7]. Such as at temperature below 573K (heating rate $<10\text{K/min}$) it undergoes an autocatalytic reaction which ceases after about 30% decomposition leaving a residue which is apparently and chemically identical with the starting material but having a larger specific surface area, this is called the low temperature decomposition reaction^[4]. Also at temperatures above 573K the so-called high temperature decomposition reaction occurs

which is not autocatalytic and goes up to complete the decomposition. Parallel to AP decomposition sublimation may take place making kinetic interpretation of AP more complex^[3].

Most of the combustion models of AP-based composite propellants used constant, determined or adjusted values for the AP decomposition kinetic parameters and the effect of its particle size over these parameters was approximately ignored. In addition, AP particle size effect was investigated from the combustion geometrical point of view only. Moreover, the heating rate effect was eliminated by using low multi-heating rate experiments to determine its decomposition kinetic parameters^[1,5-6].

In the present study, the decomposition kinetic parameters were defined as the AP required values (such as activation energy and pre-exponential factor) for the direct application over a modified Beckstead, Derr and Price (BDP) model^[2] to evaluate the ballistic properties for multi-modal AP-based composite solid propellant for-

Received: 2011-06-17; URL: www.cnki.net/kcms/detail/11.2297.V.20120525.1516.201205.1179_031.html

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mulations. Thermal analytical measurements (TAM) with one heating rate of 40 K/min were applied over AP samples with different particle sizes. In addition, their specific surface areas were measured by the multi-point Brunauer-Emmett-Teller (BET) method. Actually, description of a simplified approach for AP kinetic parameters determination represented our main objective which can be applied when a new source AP would be used for composite propellant formulations developments to evaluate their ballistic characteristics.

1 Experimental

Five AP samples with different particle sizes (purity $>99\%$ and inhibited with 0.15% anti-caking material, tri-calcium phosphate) supplied by Aldrich Chemicals Company Limited in vacuum sealed tubes. The samples were prepared by US-standard sieves except sample No. 1 by grinding. Malvern mastersizer (MSX-model) was used for AP samples particle size measurements. This instrument is able to measure the particle sizes in the range from $0.1\mu\text{m}$ to $600\mu\text{m}$ with an accuracy of $\pm 2\%$ according to volume median diameter. The measured particle sizes of the AP samples from sample No. 1 to sample No. 5 were approximately 10, 22.5, 82.5, 196, and $390\mu\text{m}$ respectively.

The thermal analytical measurements were applied using a simultaneous analyzer SDT-Q600 V20.5 (accompanied with the Universal Analysis 2000 data acquisition system). The apparatus was calibrated by indium. The tests were carried out under high purity nitrogen gas flow of 50 mL/min by using AP sample mass of about 15 mg and closed alumina sample pan. Experiments applied under one heating rate of 40 K/min, which represented the maximum allowable heating rate of the SDT-Q600 apparatus.

The specific surface areas measurements were applied by using the NOVA 2200e-WIN2 V2.1 device with nitrogen gas. The tested samples were charged one by one in the apparatus and exposed to drying under vacuum with prede-

finied temperature and time then cooled to the normal conditions followed by automatic identification of the sample weight before starting the surface area measurement. The multi-point BET method with low analysis technique (LAT) was used where the advantages of minimum surface and sample weight were enabled.

2 Methods, results, and discussions

The AP samples DSC/TGA (differential scanning calorimetry/thermal gravimetric analysis) curves (Figures 1 and 2) showed one endothermic peak at about 530 K and two exothermic peaks (except for samples No. 1 and No. 2 had only one peak) with the maximum at about 603 K and 734 K respectively. The first endothermic peak was not accompanied by any visible step wise in the mass loss, corresponded to the AP transition from the orthorhombic to the cubic phase. Exothermic peaks corresponded to the low-temperature and high-temperature decomposition. In addition, samples No. 1 and No. 2 exhibited only one weight loss step which was due to their high specific surface areas compared to

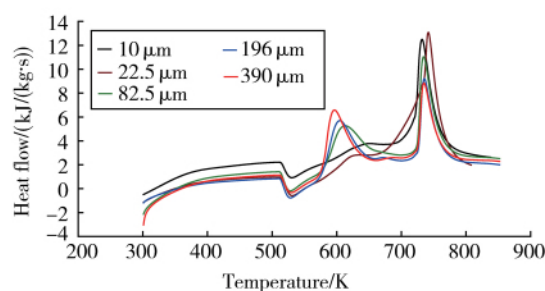


Fig. 1 AP heat flow profiles versus temperature with different particle sizes at 40 K/min

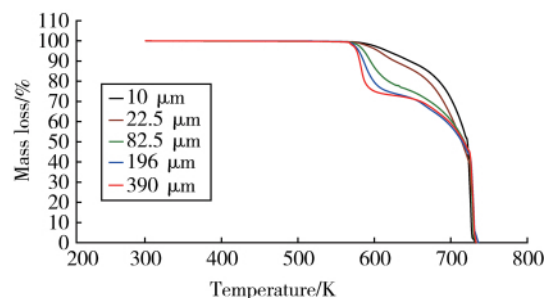


Fig. 2 AP mass loss profiles versus temperature with different particle sizes at 40 K/min

the other samples and the highly applied heating rate (40 K/min) led to shifting of the second DSC peak to the third one. On the other hand, the behavior of the other samples exhibited two weight loss steps that eliminated with decreasing the particle size from sample No. 5 to sample No. 3, which corresponded to the second DSC exothermic peaks.

Determination of the AP samples decomposition kinetic parameters started from the direct inspection over their TGA data by using the modifications applied to the basic isoconversional method. Analysis of numerous investigations showed that different kinetic equations with different approaches were applied to derive AP kinetic parameters and describe its decomposition mechanisms. The basic isoconversional method has been used for the description of many complex processes where many chemical reactions are running simultaneously however, their mechanisms are not exactly known. The basic isoconversional method can be generally described as follows^[8].

1) The mass loss data from TGA can be recalculated into conversion which is defined as

$$\alpha_i^* = \frac{m_0 - m_i}{m_0 - m_\infty} \quad (1)$$

Where; m_0 is the sample initial mass, m_i is the sample actual mass at instant i , m_∞ is the residual mass after decomposition and α_i^* is the reaction extent at instant i .

2) The rate of decomposition is a function of temperature $k(T)$ and conversion $f(\alpha^*)$:

$$\frac{d\alpha^*}{dt} = k(T) \cdot f(\alpha^*) \quad (2)$$

Where;

$$k(T) = A \cdot \exp\left(\frac{-E}{RT}\right) \quad (3)$$

$$f(\alpha^*) = (1 - \alpha^*)^\delta \quad (4)$$

Then by combining the last three equations, the decomposition kinetic equation is obtained

$$\frac{d\alpha^*}{dt} = A \cdot \exp\left(\frac{-E}{RT}\right) \cdot (1 - \alpha^*)^\delta \quad (5)$$

Where; δ is the reaction order, R is the universal gas constant, T is the actual sample temperature within a heating rate β and time t , and $k(T)$ is

the reaction rate constant.

3) According to the basic isoconversional method, decomposition kinetic parameters as the pre-exponential factor and the activation energy are not constant for the whole decomposition process but they are (apparent values) dependent on conversion. Then equation (5) is rewritten as

$$\frac{d\alpha^*}{dt} = A(\alpha^*) \cdot \exp\left(\frac{-E(\alpha^*)}{RT}\right) \cdot (1 - \alpha^*)^\delta \quad (6)$$

Thus, when solve it for a given conversion the rate of decomposition is

$$\left(\frac{d\alpha^*}{dt}\right)_{\alpha^*} = A_{\alpha^*} \cdot \exp\left(\frac{-E_{\alpha^*}}{RT_{\alpha^*}}\right) \cdot (1 - \alpha^*)^\delta \quad (7)$$

Where; A_{α^*} is the apparent pre-exponential factor, E_{α^*} is the apparent activation energy and T_{α^*} is the temperature (at the given value of conversion α^*).

4) The logarithm form of equation (7) is shown by the equation:

$$\ln\left(\frac{d\alpha^*}{dt}\right)_{\alpha^*} = \ln A_{\alpha^*} + \delta \ln(1 - \alpha^*) - \frac{E_{\alpha^*}}{RT_{\alpha^*}} \quad (8)$$

Then, in case of samples measured with multi-heating rates, for each value of conversion there is more than one decomposition rate belonging to different temperature. According to equation (8), these points approximately lie on the same line. The first two terms on the right hand side of equation (8) represent an intercept of a straight line and the term $E_{\alpha^*}/RT_{\alpha^*}$ represents a slope. Because the value of the intercept is dependent on the pre-exponential factor A_{α^*} and the reaction order δ then for the determination of the pre-exponential factor the reaction order must be identified.

In the present work, the samples were measured using one heating rate of 40 K/min. Therefore, the isoconversional method modifications were applied over each TGA run as follows^[9-10]:

1) To estimate the decomposition kinetic parameters from only one TGA run, the ap-

proach based on the assumption of an ideal system was applied. Where the decomposition kinetics of solids are customarily described by equation (5).

2) Assuming a first order process ($\delta = 1$)^[11], considering $k(T)$ from equation (2) and taking the natural logarithm of equation (3) shows:

$$\ln k(T) = \ln \left(\frac{d\alpha^*}{dt} \right) - \ln(1 - \alpha^*) = \ln A_{a^*} - \frac{E_{a^*}}{RT_{a^*}} \quad (9)$$

3) Thermal decomposition of solid materials is known to involve multiple steps with different activation energies. Then, the contributions of these steps into the overall decomposition rate measured by TGA should vary with both temperature and the degree of conversion. This means that the apparent activation energy determined from TGA experiments will be a function of these variables. Arrhenius plot of $\ln k(T)$ versus $1/T_{a^*}$ should give a straight line and the kinetic parameters are obtained from the slope (E_{a^*}/RT_{a^*}) and the intercept ($\ln A_{a^*}$).

A FORTRAN computer program was designed to calculate the data required, $\ln k(T)$ and ($1/T_{a^*}$). For each run, the calculated data was inspected (filtered and re-tabulated versus 5% conversion to about 70% conversion) then linearly fitted as a straight line equation to calculate the kinetic parameters. The program input data file was the measured TGA data for each sample between 1% and 99% decomposition. It is considered that the determined kinetic parameters using the previous scheme represented the low

conversion values at 5% to 30% and the high conversion values at 30% to 70%. In addition, the 30% conversion represented the reference value at the range of about 663–703 K, from sample No. 5 to sample No. 1 respectively. The Plotter 7.7 Software was used to fit the Arrhenius plot data for each sample (through three steps) as shown in appendix-A for sample No. 1. The samples reaction rate constant behaviors (from low to high conversions) are shown in Figure 3. The determined kinetic parameters of AP samples in comparison with the measured specific surface areas are presented at Table 1. It is clear that the higher the particle size the lower the measured specific surface area.

Our TGA measurements had shown some difficulty to catch the induction at temperatures above 723 K because the induction period was too short and the decomposition proceeded so rapidly. This made the kinetic treatment of the obtained data more complex and accordingly the obtained kinetic parameters values to be less reliable. So we had limited our determinations up to

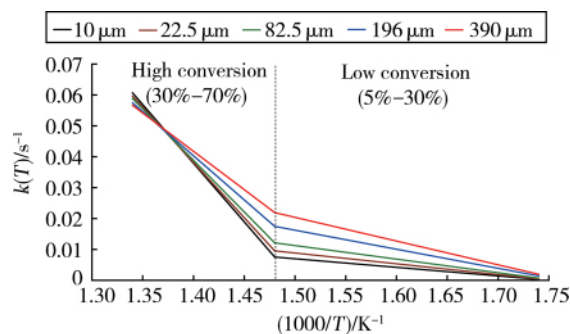


Fig. 3 AP reaction rate constant behavior with different particle sizes

Table 1 Measured and determined results of AP samples

Sample No.	Average particle size/ μm	Specific surface/ (m^2/g)	(5%–30%)		(30%–70%)	
			$A_{a^*}/10^5 \text{ s}^{-1}$	$E_{a^*}/(\text{kJ/mol})$	$A_{a^*}/10^6 \text{ s}^{-1}$	$E_{a^*}/(\text{kJ/mol})$
1	10	0.56	5.16	101.58	5.14	113.51
2	22.5	0.37	2.52	96.22	4.66	113.01
3	82.5	0.19	1.21	90.73	3.86	111.92
4	196	0.13	0.286	80.56	3.25	111.00
5	390	0.09	0.207	77.46	3.14	110.87

70% conversion.

However, there were considerable variations of the AP activation energy values in literature ranged from 71 to 172 kJ/mol^[3-7] they were matched with the present activation energy determinations. Some of these variations were undoubtedly due to the widely different kinetic analysis employed in the decomposition kinetic parameters derivation. In addition, although the reaction order δ was assumed to be equal one [$\delta(\text{AP}) \approx 1.8$] the AP kinetic parameters determined by Kissinger method for different AP particle sizes were in good agreements when compared with our determinations^[12].

Hence, the decomposition kinetic parameters determinations for the AP samples under investigation were reasonable because the higher the AP particle sizes the lower the pre-exponential factor and activation energy (especially) at the low conversion interval due to the clear decrease accompanying AP specific surface areas. Also the same behavior was verified at the high conversion interval but, the difference between the values can be neglected when compared to the later interval because the remained AP melted in a thin (few microns) superficial liquid layer and created an exothermic reaction affected the remainder AP (30%) to sublime into NH_3 and HClO_4 which reacted exothermically in a premixed flame very close to the surface^[1,5-6].

3 Conclusions

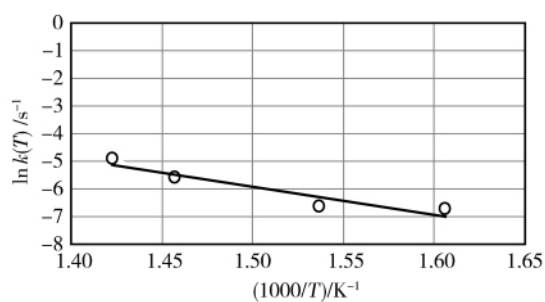
Each simultaneous DSC/TGA run for AP could be treated separately to determine the decomposition kinetic parameters using the modified approach based on the isoconversional method. The effect of AP particle sizes variation (10–390 μm) on the decomposition kinetic parameters under one heating rate (40 K/min) was clear. At the low conversion interval when the particle size was lowered from 390 μm to 10 μm (specific surface increased by about 6.2-fold) the activation energy and pre-exponential factor increased by about 1.3-fold and 24.9-fold re-

spectively. The reaction rate constant $k(T)$ at 673 K decreased by about 65%. Moreover, the extrapolated reaction rate constant $k(T)$ at 743 K increased by about 7% only at the high conversion interval. So it was recommended to introduce the decomposition kinetic parameters variations at high conversion based on their particle sizes and specific surface areas when applied upon the multi-modal AP-based composite propellants combustion.

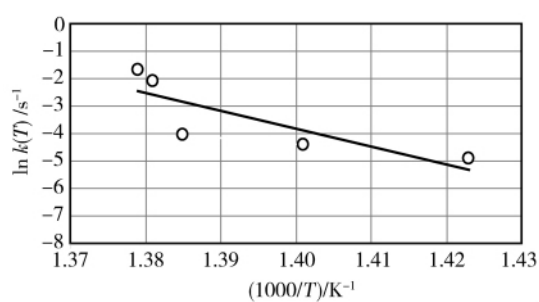
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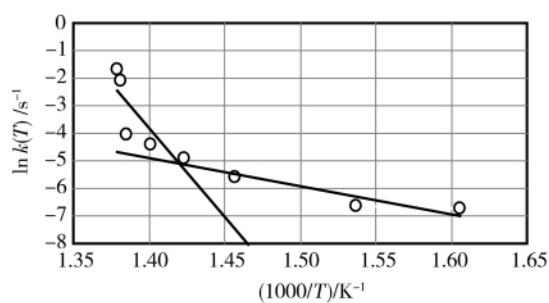
Appendix:



(a) Sample No. 1 arrhenius plot at low conversion
(5%, 10%, 20%, and 30%)



(b) Sample No. 1 arrhenius plot at high conversion
(30%, 40%, 50%, 60% and 70%)



(c) Sample No. 1 arrhenius plots from low
to high conversions