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Thermal Behavior of Non-explosive and Irrestorable Fertilizer-grade Ammonium Nitrate

SHEN Li-jin[1,2], **MA Ai-e**[3], **WANG Xu-guang**[1,4], **WANG Ping**[1]

(1. *China Society of Engineering Blasting*, *Beijing* 100142, *China*; 2. *China Metallurgical Industry Planning and Research Institute*, *Beijing* 100711, *China*; 3. *Beijing Institute of Space Long March Vehicle*, *Beijing* 100076, *China*; 4. *Beijing General Research Institute of Mining and Metallurgy*, *Beijing* 100160, *China*)

Abstract: To analyze and compare the thermal stability of commercial ammonium nitrate (AN) and homemade non-explosive and irrestorable fertilizer-grade ammonium nitrate (NEIFAN), the crystal transformation changes, thermal decomposition characteristics and adiabatic decomposition processes of AN and NEIFAN were studied by thermogravimetry(TG)-differential thermal analysic(DTA)-derivative thermogravimetry(DTG), differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC). The curves of thermal decomposition temperature and pressure vs time, self-heating rate and pressure vs temperature for AN and NEIFAN under the adiabatic decompositions condition were obtained. The kinetic parameters (apparent activation energy and pre-exponential factor) of pseudo zero order adiabatic decomposition reaction for AN and NEIFAN were calculated. The results show that in comparison with AN, the crystal transformation peak at about 88 ℃ of NEIFAN disappears, revealing that NEIFAN has better thermal physical stability. The decomposition peak temperature of NEIFAN obtained by TA-DTA-DTG and DSC curves and the apparent activation energy of the pseudo zero order adiabatic decomposition reaction of NEIFAN obtained by ARC data are much higher than those of AN, indicating that NEIFAN has a higher heat-resistance ability than AN. Considering that the increase of physicochemical stability of NEIFAN is attributed to the joint action of inorganic and organic additives in NEIFAN.

Key words: analytical chemistry; ammonium nitrate; non-explosive and irrestorable fertilizer-grade ammonium nitrate; thermal analysis; thermal stability

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1 Introduction

The non-explosive and irrestorable fertilizer-grade ammonium nitrate (NEIFAN) is a kind of modified ammonium nitrate (AN), which is composed of AN and anti-explosive additives[1-3]. Its preparation and properties have been reported[2]. However, its thermal stability and adiabatic decomposition reaction kinetics have not yet been reported. The aim of this work is to study the thermal behavior and thermal safety of NEIFAN by thermogravimetry-differential thermal analysis (TG-DTA), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC). It is quite useful in the evaluation of its heat-resistance ability and thermal safety under non-isothermal and adiabatic conditions and in the better understands of its phenomenon, mechanism, and process from thermal decomposition and adiabatic decomposition to thermal explosion[2].

2 Experimental

2.1 Samples

Ammonium nitrate used in the experiment was of chemical purity. It was a commercial product of Liu-li dian chemical plant, Beijing, with purity higher than 98%. Its density and particle diameter (d_{50}) were 1.72 g · cm^{-3} and 100–150 μm, respectively[2];

Non-explosive and irrestorable fertilizer-grade ammonium nitrate (NEIFAN) with 8% anti-explosive additives as anti-explosive agents was from Beijing General Research Institute of Mining and Metallurgy[2,4-6]. The measured values for density and particle diameter (d_{50}) were 1.83 g · cm^{-3} and 140 μm, respectively[2].

2.2 Apparatus and test conditions

TG-DTA tests were carried out on a SDT2960 V3. OF TA instrument. The operation conditions of TG-DTA were: pan, closed cell of aluminum; atmosphere, a flowing rate of 40 mL · min^{-1} of air; heating rate, 2.5 ℃ · min^{-1}; temperature range, 25–500 ℃. DSC tests were performed on a MDSC instrument (Model TA2910 V4.4E TA Co. USA) The operation conditions of DSC were as follows: pan, closed cell of aluminum; atmosphere, a flowing rate of 40 mL · min^{-1} of N_2; heating rate, 2.5 ℃ · min^{-1}. Temperature calibrating of DTA and TG-TGA curves in the range of 25–500 ℃ were performed by running melting standards. In order to obtain calorimetric results, the same standards were used to calibrate the temperature of DSC curve. These calibrations were performed at a heating rate of 2.5 K · min^{-1} by using a sample size of (3.71±0.05) mg. The gain of the thermobalance was chosen to give an approximate resolution of 0.3 μg. The samples were loaded into open alumina crucibles and a dry nitrogen purge flow of 40 mL · min^{-1} at 0.1 MPa absolute pressure was used ARC measurements were made with an accelerating rate calorimeter manufactured by Columbia Scientific Industries and operated according to the conditions shown in Table 1[7]. The principle and method of collecting, analyzing and treating the data from ARC curves and the corrected method of inertia factor Φ were same as those in Refs. [7–8].

3 Results and discussion

3.1 Thermal decomposition behavior of AN and NEIFAN under non-isothermal conditions

The TG-DTA-DTG curves of AN and NEIFAN are shown

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Biography: SHEN Li-jin (1971–), male, Ph. D. senior engineer, research fields: industrial explosive and blasting technology, mining engineering.
e-mail: cliffslj@163.com

in Fig. 1 and Fig. 2. The DTA curves of AN consists of three crystal transformation peaks at 53.45, 88.06, 126.03 ℃, one melting peak at 168.69 ℃ and one decomposition peak at 234.93 ℃. The DTA curve of NEIFAN consists of two crystal transformation peaks at 52.91, 127.16 ℃, one melting peak at 168.47 ℃ and one decomposition peak at 263.87 ℃. The phase transformation peak at about 88 ℃ disappears, which is attributed to the joint action of inorganic and organic additives in NEIFAN. The peak temperature of decomposition reaction for NEIFAN is much higher than that of decomposition reaction for AN, showing that the thermal stability of NEIFAN is better than that of AN. The DSC curves of two samples are shown in Fig. 3 and Fig. 4, which are similar to the DTA curves in Fig. 1 and Fig. 2. Mass loss processes of AN and NEIFAN with temperature under non-isothermal conditions show only one stage on TG and TGA curves.

Table 1 Mass of samples and measuring conditions in ARC

characteristic parameters	AN	NEIFAN
sample mass, m/g	0.367	0.504
bomb mass, m_b/g	6.380	6.804
starting temperature, $T_{0,s}$/℃	150	150
slope sensitivity/℃ · min^{-1}	0.02	0.02
heat step temperature/℃	3	3
wait time, t/min	5	5

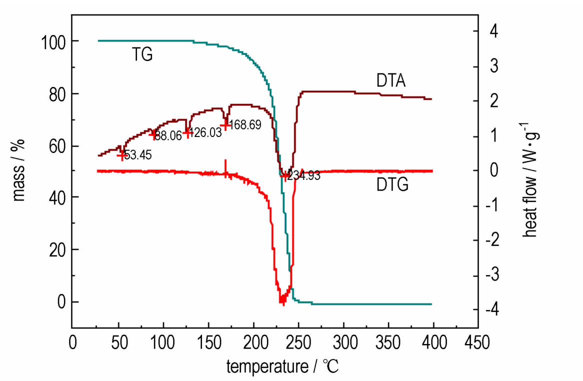

Fig. 1 TG-DTA-DTG curves for AN

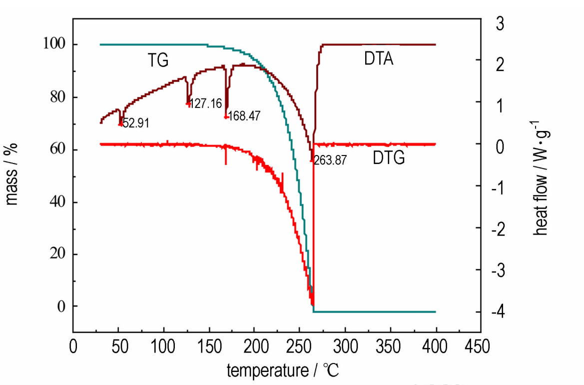

Fig. 2 TG-DTA-DTG curves for NEIFAN

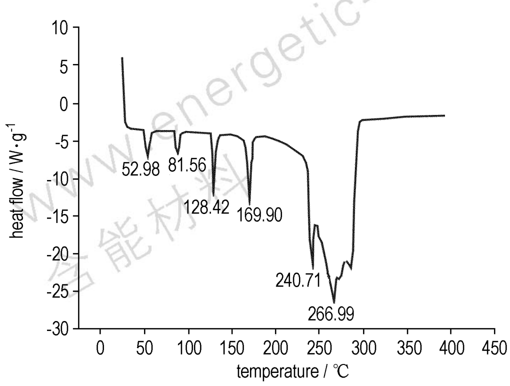

Fig. 3 DSC curve for AN

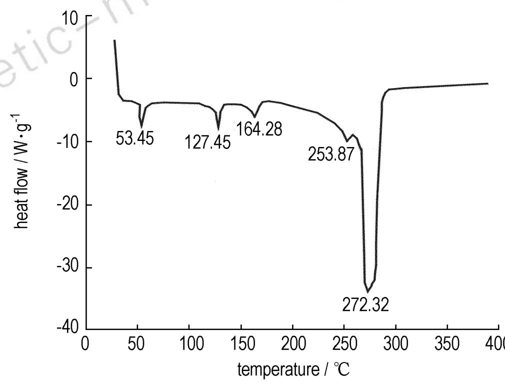

Fig. 4 DSC curve for NEIFAN

3.2 Thermal decomposition behavior of AN and NEIFAN under adiabatic conditions

Time-temperature-pressure curves for AN and NEIFAN are shown in Fig. 5. The test results and the derived adiabatic decomposition reaction characteristic data of AN and are summarized in Table 2. The curves of self-heating rate vs. temperature of AN and NEIFAN are shown in Fig. 6 and Fig. 7. The curves of the pseudo rate constant k as a function of temperature for the adiabatic decomposition reaction of AN and NEIFAN obtained by Eqs. (1), (2) and (3) are shown in Fig. 8 and Fig. 9. The apparent activation energy and pre-exponential constant of the pseudo zero order adiabatic decomposition reaction of AN and NEIFAN obtained by ARC data from Fig. 5–Fig. 7 and the calculated values of pseudo zero-order rate constant at 360 ℃[9], $k_{360\ ℃}$ are listed in Table 3.

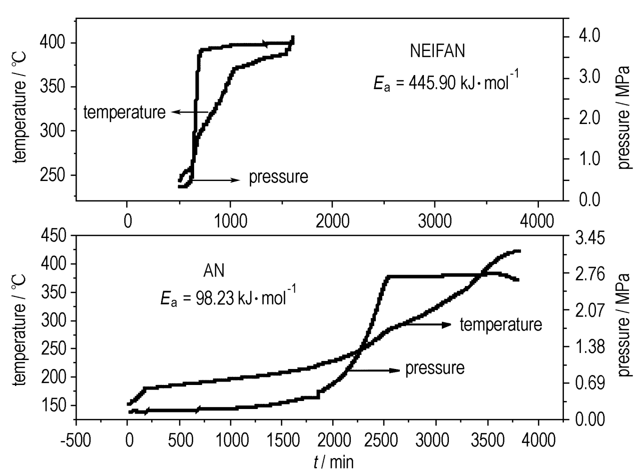

Fig. 5 Time-temperature-pressure curves of AN and NEIFAN

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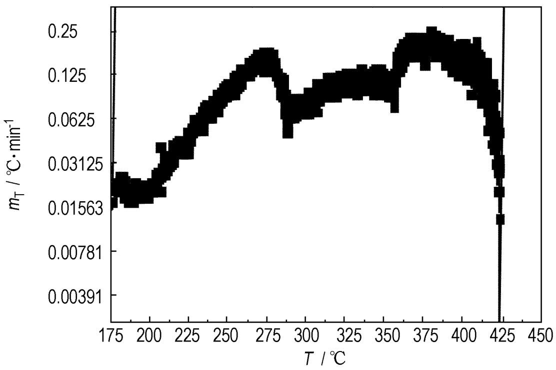

Fig.6 The T VS. M_T curve of AN

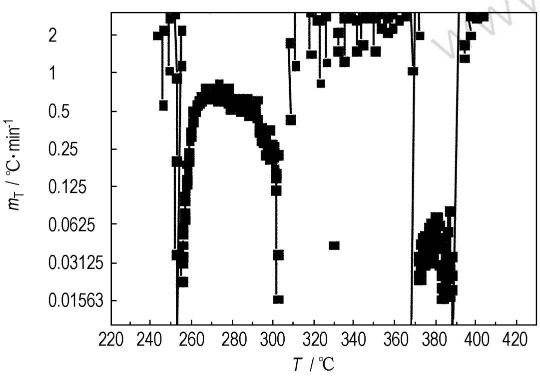

Fig.7 The T VS. M_T curve of NEIFAN

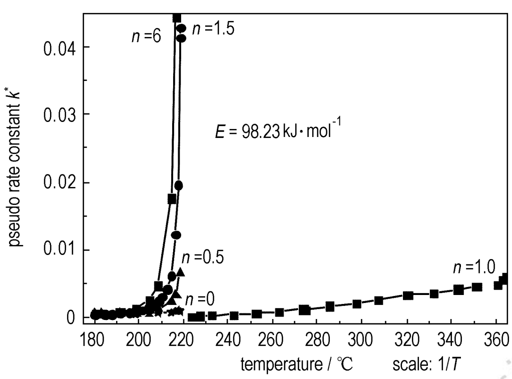

Fig.8 The k^* vs. T curves of AN

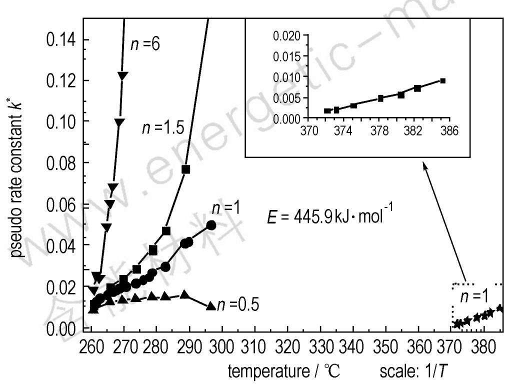

Fig.9 The k^* vs. T curves of NEIFAN

Table 2 Measured thermal decomposition characteristic data of AN and NEIFAN

characteristic parameter	AN	NEIFAN
sample mass, m/g	0.367	0.504
inertia factor, Φ	5.875	4.550
onset temperature, $T_{0,s}$/℃	180.47	255.65
self-heat rate, $m_{0,s}$/℃ · min^{-1}	0.022	0.031
maximum self-heat rate, $m_{m,s}$/℃ · min^{-1}	0.04	0.14
maximum self-heat rate, $m_{m,s}$/℃ · min^{-1} (Φcorrected)	0.16	0.641
final temperature, $T_{f,s}$/℃	287.51	388.12
final temperature, $T_{f,s}$(Φcorrected)/℃	809.33	858.39
adiabatic temperature rise, ΔT_{ad}/℃	107.04	132.47
adiabatic temperature rise, ΔT_{ad}/℃ (Φcorrected)	628.86	602.74
time to maxiumum rate, $\theta_{m,s}$/min	1252.90	43.18
time to maxiumum rate, $\theta_{m,s}$/min (Φcorrected)	213.26	9.49
temperature at maximum self-heat rate, $T_{m,s}$/℃	273.59	267.65
maximum pressure rise, $p_{m,s}$/MPa	2.69	3.86

Table 3 The kinetic parameters of the pseudo zero order adiabatic decomposition reaction of AN and NEIFAN

samples	A/s^{-1}	E/kJ · mol^{-1}	$k^*_{360\,℃}$/s^{-1}
AN	3.5×10^{17}	98.23	$10^{9.44}$
NEIFAN	2.75×10^{42}	445.90	$10^{5.64}$

Note: 1) k^* is a pseudo zero-order rate constant at 360 ℃.

$$\ln k^* = \ln C_0^{n-1} A - \frac{E}{R}\left(\frac{1}{T}\right) \quad (1)$$

$$k^* = C_0^{n-1} k = \frac{m_T}{\Delta T_{ad}\left(\frac{T_{f,s}-T}{T_{ad}}\right)^n} \quad (2)$$

$$m_T = \frac{dT}{dt} = k\left(\frac{T_{f,s}-T}{T_{f,s}-T_{0,s}}\right)^n \Delta T_{ad} C_0^{n-1} \quad (3)$$

Where k^* is a pseudo zero-order rate constant at temperature T, ℃; n is reaction order; C_0 is the initial concentration of the reactant; A is the pre-exponential constant, s^{-1}; E is the apparent activation energy, kJ · mol^{-1}; $T_{f,s}$ is the final temperature, ℃; $T_{0,s}$ is the initial temperature, ℃; $T_{f,s}-T_{0,s}$ is the adiabatic temperature rise, ΔT_{ad}[10-11], ℃.

Fig. 5 – Fig. 9 and Tables 2 and 3, the following observations can be made.

(1) The adiabatic decomposition process can be derived into two exothermal stages

(2) The adiabatic decomposition reactions of AN and NEIFAN are exothermic, whereas the two reactions performed in non-sealed DSC conditions are endothermic.

(3) The facts of $T_{0,s}$(NEIFAN) > $T_{0,s}$(AN), $T_{f,s}$(NEIFAN) > $T_{f,s}$(AN), $T_{f,s}$(Φcorrected, NEIFAN) > $T_{f,s}$(Φcorrected, AN), E(NEIFAN) > E(AN) and $k_{360\,℃}$(NEIFAN) < $k_{360\,℃}$(AN) indicate that the thermal stability of NEIFAN is better than that of AN.

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(4) Using ΔT_{ad} (Φ corrected) as criterion, the thermal safety of AN and NEIFAN decreases in the order of NEIFAN> AN.

(5) The kinetic equation describing the adiabatic decomposition reaction in studied temperature range is

for AN.

$\ln k^* = 40.35 - 11815/T$

for NEIFAN

$\ln k^* = 97.61 - 53632/T$

4 Conclusion

(1) The decomposition reactions of AN and NEIFAN in adiabatic and sealed system are exothermic, whereas the two reactions performed in non-sealed DSC conditions are endothermic.

(2) Using the peak temperature of decomposition reaction and the apparent activation energy of adiabatic pseudo zero order decomposition reaction as criterions, the heat-resistant abilities of AN and NEIFAN decrease in the order of NEIFAN>AN, showing that NEIFAN has better thermal stability than AN.

(3) In comparison with AN, the disappearance of the phase transformation peak at about 88 ℃ of NEIFAN means that NEIFAN has better thermal physical stability.

(4) The relations of thermal decomposition temperature and pressure versus time, self-heating rate and pressure versus temperature describing the adiabatic decomposition reaction for AN and NEIFAN were presented.

(5) The increase of physicochemical stability of NEIFAN is due to the joint action of inorganic and organic additives in NEIFAN.

(6) The adiabatic decomposition processes of AN and NEIFAN accord with the pseudo zero order reaction theory model.

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非爆炸且不可还原农用硝酸铵的热行为

沈立晋[1,2]，马爱娥[3]，汪旭光[1,4]，汪　平[1]

(1. 中国工程爆破协会，北京 100142；2. 冶金工业规划研究院，北京 100711；3. 北京航天长征飞行器研究所，北京 100076；4. 北京矿冶研究总院，北京 100160)

摘　要：为分析、比较商用硝酸铵(AN)和自制非爆炸/不可还原农用硝酸铵(NEIFAN)的热稳定性，用热重(TA)-差热扫描量热(DTA)-微商热重(DTG)、差示扫描量热(DSC)和绝热量热(ARC)研究了 AN 和 NEIFAN 的晶转变化、热分解特性和绝热分解过程，得到了绝热分解温度与压力随时间、自加热速率与分解压力随温度的变化曲线，计算了绝热假零级分解反应动力学参数——表观活化能和指前因子。结果表明，与 AN 相比，NEIFAN 在 88 ℃左右的晶转峰消失，显示 NEIFAN 有更好的热物理稳定性。由 TA-DTA-DTG和 DSC 曲线所得的 NEIFAN 的热分解峰温度和由 ARC 数据所得的 NEIFAN 的假零级绝热分解反应的表观活化能比 AN 的相应值高，表明 NEIFAN 比 AN 有更好的热稳定性。认为，NEIFAN 的物理化学稳定性的提高应归因于 NEIFAN 中无机和有机添加剂的联合作用。

关键词：分析化学；硝酸铵；非爆炸且不可还原农用硝酸铵；热分析；热稳定性

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