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Preparation of Metallic Amorphous Al/Ti Spherical Particles and Their Catalysis Effects on the Thermal Decomposition of High Explosives

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Abstract: By controlling the milling time and the mass proportion of Al to Ti, the metallic amorphous Al/Ti spherical particles (Al/Ti alloy) with a mean size of 3.76 μm were fabricated by mechanical milling method. The catalysis effects of the as-prepared Al/Ti alloy on the thermolysis of five explosives, namely hexanitrostilbene (HNS), 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105), cyclotrimethyltrinitroamine (RDX), cyclotetramethylenetetranilamine (HMX), and hexanitrohexaazaisowurtzitane (CL-20) were probed by thermal analysis. Results show that for HNS doped with 5wt% Al/Ti particles, the decomposition peak temperature (T_p) decreases by 6.9, 7.2, 4.8 and 5.2 °C at different heating rates compared with raw HNS. Similarly, for the rest four explosives, the T_p value of the doped explosives also decreases compared with the respective raw explosive. All thermodynamic parameters of the explosives were calculated. It is indicated that the active energy (E_K) of the doped explosives is declined by 52.378 kJ·mol^{-1} (HNS), 41.664 kJ·mol^{-1}, (LLM-105), 8.6 kJ·mol^{-1} (RDX), 48.4 kJ·mol^{-1} (HMX), and 46.7 kJ·mol^{-1} (CL-20). It is ascertained that doping spherical amorphous Al/Ti alloy can promote the thermal decomposition of explosives.

Key words: ball mill; Al/Ti alloy; catalysis; thermal decomposition; high explosive

Al powder is an indispensable metal fuel in propellants and explosives [1-3]. It can release a great mass of heat when burned. Its density is obviously higher than that of the traditional CHNO explosives. Accordingly, the charge density of ammunition will be significantly enhanced by adding Al powder. However, a compact oxide layer on the surface of micro-Al particles severely inhibits the reaction and leads to an enormous activity reduction [4-6]. In the past 20 years, there have been many reports about how to promote the activity of micron Al. Wang et al used in-situ displacement method to coat nano metal particles (Cu, Ni, Co and Fe) on the surface of micro-Al particles to form nanocomposites with core-shell structure [7-13]. These Al-based nanocomposites have higher reactivity than micron Al powders. But this way has two lacks, namely the limited reaction improvement and the small quantity preparation of nanocomposites.

Alloying Al with other metals such as Mg is another way to improve its reactivity [14-16]. For example, Wang prepared Al/Mg alloy by ball milling, and studied the impact initiation characteristics of the Al/Mg alloy based thermite [17,18]. It reveals that the thermite with higher reactivity is easily ignited by high-speed impact and then ignites the diesel oil in the target tank. However, Mg is of great activity, and is very easy to be severely corroded by water or steam when exposed in air, especially in batch preparation of the Mg based alloy. Therefore, it is not the best way to improve the activity of micro Al.

Metallic Ti with a higher heat and stability has entered our vision [19]. In this study, the spherical amorphous Al/Ti alloy was prepared by ball mill and its catalysis effect on the

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thermal decomposition of high explosives was thoroughly investigated. Firstly, the ball milling can significantly refine the Al particles, and the presence of Ti can eliminate the Al oxide layer. Accordingly, the reactivity of Al can be greatly improved. Next, the spherical amorphous Al/Ti alloy was prepared by ball milling. As we know, the amorphous alloy is better than its crystalline due to its lower ignition temperature and higher burning rate. However, it is difficult to obtain metallic and amorphous Al/Ti spherical particles. Based on the above, the Al/Ti alloy is expected to be used in advanced explosives and solid propellants. Thus, it is very important to investigate the interaction between Al/Ti alloy and high explosives.

1 Experiment

1.1 Materials

Raw Al powder was purchased from China Ocean Aluminum Co., Ltd. Raw Ti powder was purchased from Yunfu Nanotechnology Co., Ltd (Shanghai, China). Stearic acid was purchased from Zhiyuan Chemical Reagent Co., Ltd (Tianjin, China). The balls were purchased from Pengfa Fasteners Co., Ltd (Wenzhou, China). HNS and HMX were purchased from Gansu Yinguang Chemical Co., Ltd. (Baiyin, Gansu Province, China). CL-20 and RDX were purchased from Beijing University of Science and Technology (Beijing, China). LLM-105 was fabricated by our laboratory.

1.2 Preparation

Raw Al powder and raw Ti powder were mixed at a certain ratio, and a given mass of milling balls were added into the mixture. The 5% stearic acid was subsequently introduced into the mixture as the milling assistant agent. All the mixture was milled at a certain speed for 40 h in a ball machine. Afterwards, the mixture was moved out from the ball machine, and the balls were completely separated from the mixture. Spherical amorphous Al/Ti alloy was obtained.

1.3 Characterization

The morphologies of the samples were observed with a field-emission scanning electron microscope (SEM, JEOL JSM-7500). The phases of the samples were investigated with an X-ray diffractometer (XRD, Bruker Advance D8) using Cu Kα radiation at 40 kV and 30 mA. Thermal analysis of the samples was performed on a differential scanning calorimeter (TA Model Q600) at heating rates of 5, 10, 15, and 20 °C·min^{-1} (N_2 atmosphere, sample mass of approximately 5 mg, and Al_2O_3 crucible).

2 Results and Discussion

2.1 Crystal phase

The structure of the Al/Ti alloy samples was analyzed by XRD. Fig. 1 depicts the curves of samples at different mill time and Al/Ti ratios. It is distinct that the intensity of the diffraction peak of Al and Ti both decrease gradually as the mill time is prolonged. Until 20 h, the Al's peaks disappear completely, while the Ti's peaks become faint. Afterwards, the peaks of Al and Ti both disappear completely at 30 and 40 h, which indicate that the alloy become amorphous. As the collisions between the balls and the alloy particles increase, the morphology of the alloy particles gradually changes from flaky to granular until the diffraction peaks completely disappear. This means that the alloy powder turns into amorphous station. Therefore, the optimum milling time is determined as 40 h.

Fig.1b shows that the peaks of Al and Ti appear simultaneously when the ratio of Al to Ti is 9/1. However, as the ratio turns to 8/2, Ti's peaks disappear, and Al's peaks remain. When ratio turns to 7/3, the peaks of Al and Ti simultaneously disappear. Afterwards, the peaks of the Al and Ti disappear with increasing the Ti. It illustrates that the alloy becomes amorphous. Therefore, the optimal ration of Al to Ti is determined as 7/3.

2.2 Micron Morphology and particle size

The morphology of the Al/Ti alloy sample as prepared under the optimum conditions is shown in Fig.2. It is distinct that the alloy particles are well dispersed, and homogeneously spherical. Their particle size is about 4 μm. Fig.2b~2d are the higher magnification images of Fig.2a. It is clear the alloy particles have quite well sphericity and homogeneity. Fig.3 shows the particle size distribution curve of the alloy particles. The alloy's frequency distribution curve (Fig.3a) is quite well consistent with its cumulative distribution curve (Fig.3b), which confirms that it has a narrow size distribution and well size homogeneity.

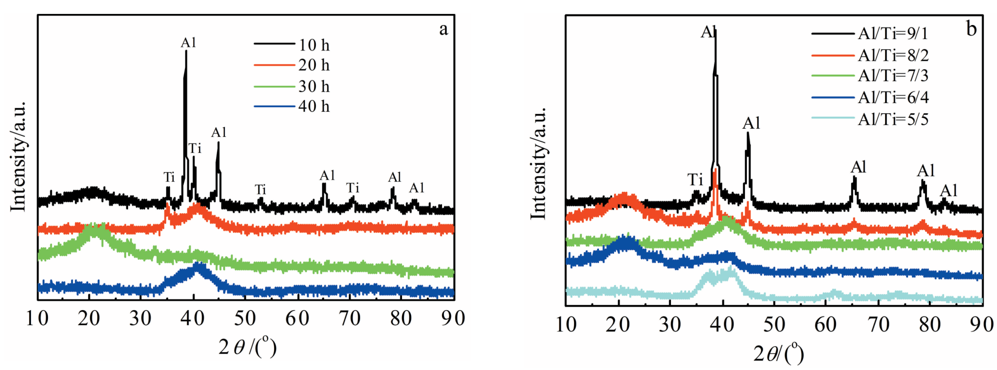

Fig.1 XRD patterns of samples at different milling time (a) and different mass ratio of Al to Ti (b)

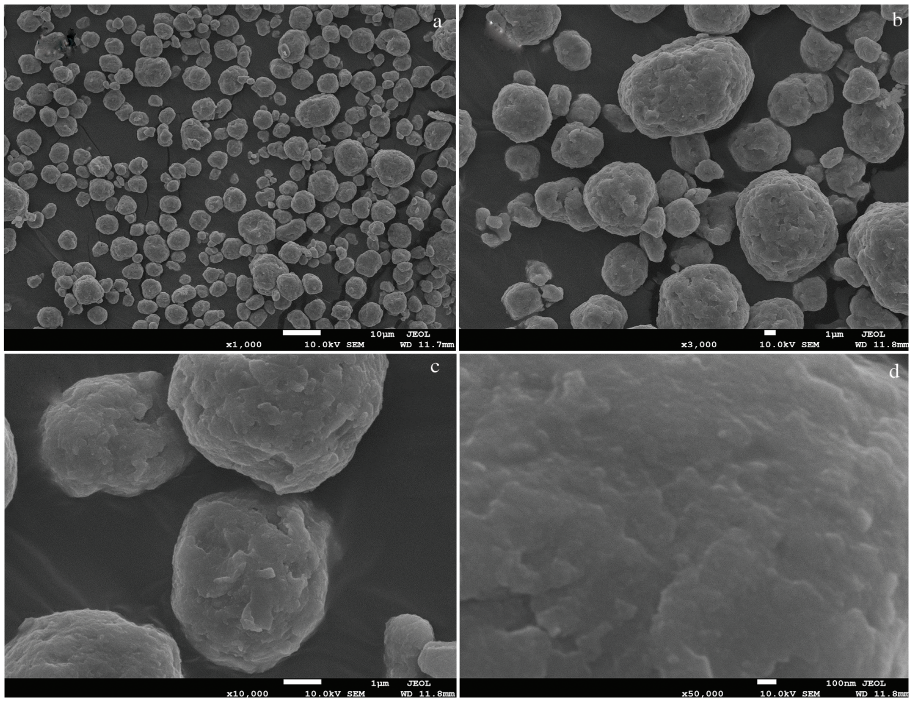

Fig.2 SEM morphologies of metallic Al/Ti composite

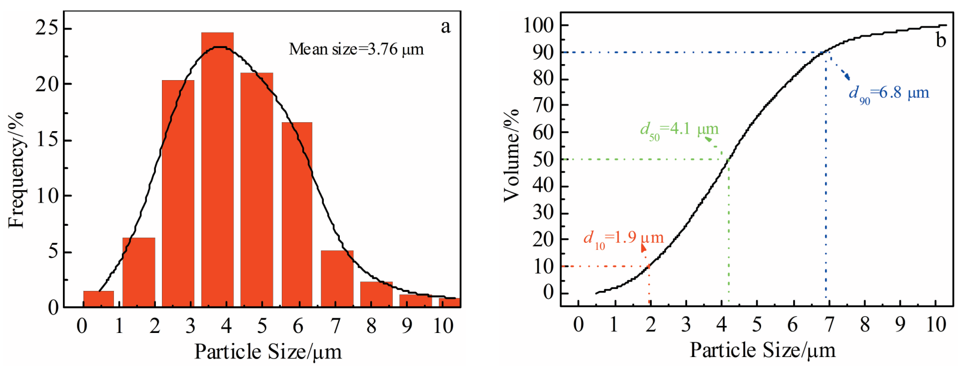

Fig.3 Particle size distribution of Al/Ti composites calculated from Fig.1a: (a) frequency curve and (b) volume curve

2.3 Catalysis effect

2.3.1 Catalysis for nitro explosives

HNS is a light yellow crystal explosive with good stability and low sensitivity, especially high heat resistance. It is very suitable for working at 260 °C. However, it has only slightly higher energy than TNT. In recent years, a new heat resistant explosive named LLM-105 has attached people's attention. The heat resistance of LLM-105 is equivalent to that of HNS, while it has higher energy as 81% of HMX, or 20% more than 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). HNS and LLM-105 are widely used in detonators, detonating cord and perforating charge, where the high temperature operation is needed. So, the Al/Ti alloy's catalysis effect on the thermal decomposition of HNS and LLM-105 is investigated in detail, as shown in Fig.4 and Fig.5.

Raw HNS has a distinct melting endothermic peak (317 °C), which is followed by rapid thermal decomposition. With rising the heating rate, HNS's decomposition peak temperature also rises. The HNS doped with Al/Ti alloy has the similar pattern, i. e. it decomposes rapidly after it melts (312 °C). Distinctly, the doped HNS melts are ahead of raw HNS by 5 °C, which also decompose in advance of the raw HNS by 6.9, 7.2, 4.8 and 5.2 °C at different heating rates. It is clear that the HNS doped with Al/Ti alloy has higher thermal reactivity than raw HNS.

Unlike HNS, LLM-105 has no melting peak and only one decomposition peak at different heating rates. The LLM-105 doped with Al/Ti alloy also decomposes in advance of raw LLM-105 by 0.5, 1.3, 1.6 and 2.1 °C at different heating rates. In order to further investigate the thermal decomposition of the explosives, the thermodynamic parameters were calcu-

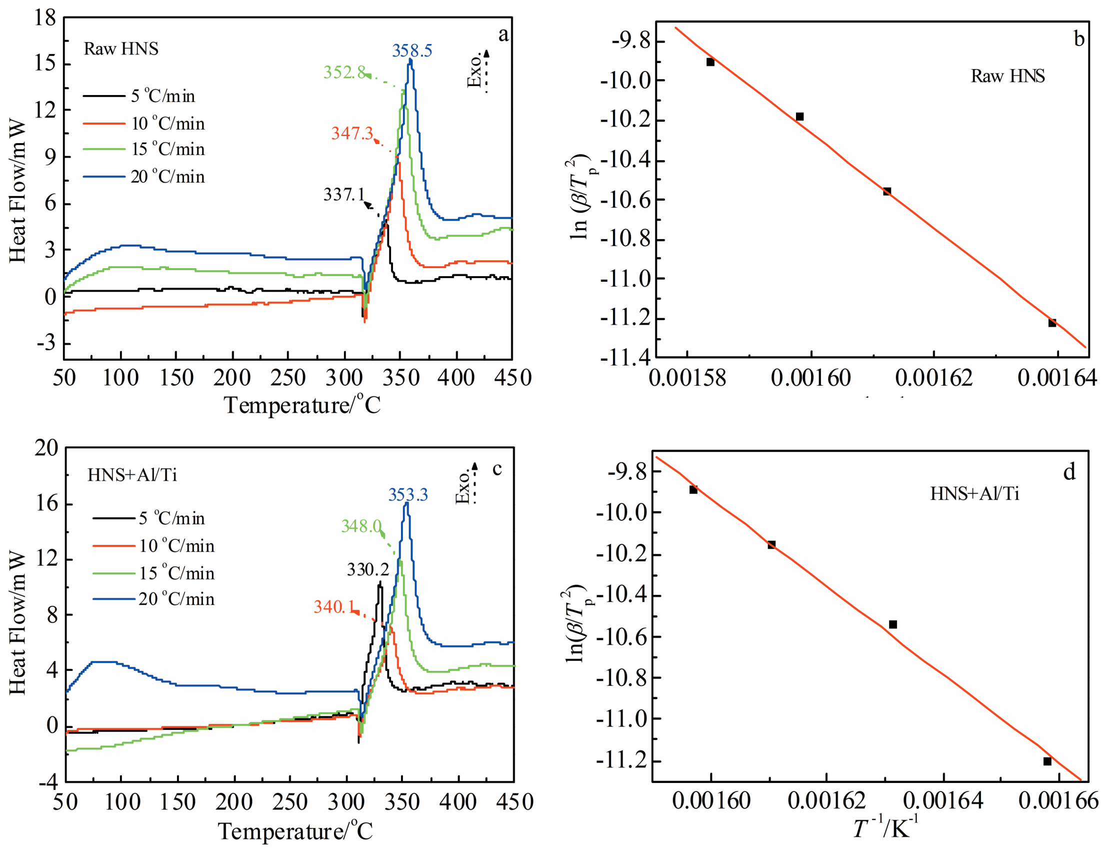

Fig.4 DSC traces of raw HNS (a, b) and HNS doped with Al/Ti composite (c, d)

lated according to Eq.(1~5), as listed in Table 1.

$$\ln\frac{\beta}{T_p^{\ 2}} = \ln\frac{R\cdot A_K}{E_K} - \frac{E_K}{R}\cdot\frac{1}{T_p} \qquad (1)$$

$$k = A_K\cdot\exp\left(-\frac{E_K}{T_p\cdot R}\right) \qquad (2)$$

$$A\exp\left(-\frac{E_K}{RT_P}\right) = \frac{K_B T_P}{h}\exp\left(-\frac{\Delta G^{\neq}}{RT_P}\right) \qquad (3)$$

$$\Delta H^{\neq} = E_K - RT_P \qquad (4)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T_P\Delta S^{\neq} \qquad (5)$$

where T_p is the peak temperature, in K; K_B and h are the Boltzmann (K_B=1.381×10^{-23} J·K^{-1}) and Plank constant (h= 6.626×10^{-34} J·s^{-1}), respectively; β is the heating rate; E_K and A_K are the activation energy and pre-exponential factor, respectively; $\Delta H^{\neq}$ is activation enthalpy, in J·mol^{-1}; $\Delta G^{\neq}$ is activation free energy, in J·mol^{-1}; $\Delta S^{\neq}$ is activation entropy, in J·mol^{-1}·K^{-1}.

Table 1 shows that both HNS and LLM-105 cannot decompose spontaneously. Their initiation needs some heats (i.e., $\Delta H^{\neq}$). According to the $\Delta H^{\neq}$ values in Table 1, the raw explosives need more heat to be activated. All $\Delta G^{\neq}$ are positive values, which confirms that the decomposition of all explosives will not be initiated spontaneously. The values of activation entropy ($\Delta S^{\neq}$) are calculated by Eq.(5). We can find that all $\Delta S^{\neq}$ are positive values. This makes the $T\cdot\Delta S^{\neq}$ term in Eq.(5) negative. Meanwhile, a positive value for $\Delta S^{\neq}$ corresponds to an increase in the randomness or disorder of the system when the activation of the molecules occurs. In particular, the E_K value of the doped explosives decreases by 52.378 kJ·mol^{-1} (HNS), 41.664 kJ·mol^{-1} (LLM-105), 8.6 kJ·mol^{-1} (RDX), 48.4 kJ·mol^{-1} (HMX), 46.7 kJ·mol^{-1} (CL-20). It reveals that the doped explosives decompose easily with less energy after adding Al/Ti alloy. It is more conducive to initiating the decomposition. The addition of Al/Ti alloy has a good promoting effect on the thermal decomposition reaction of HNS and LLM-105.

2.3.2 Catalysis for nitroamine explosive

Nitroamine explosives are widely used as energy additives in the formulas of propellants and mixed explosives. RDX is well known as a typical nitroamine explosive with high energy, moderate sensitivity, and low cost. It is of mass use in ammunition. HMX is another famous nitroamine explosive for its high energy, moderate sensitivity, and outstanding comprehensive performance. In recent years, CL-20, as the highest nitroamine explosive, has been used in propellants and mixed explosives. Therefore, how the Al/Ti alloy acts on the thermal decomposition of these nitroamine explosives is necessary to be thoroughly investigated.

Fig.6 is the DSC traces of raw RDX and RDX doped with Al/Ti composite. For raw RDX, its melting peak remains unchanged with rising the heating rate, but its decomposition peak temperature rises by 19.3 °C from 5 °C/min to 20 °C/min. Raw RDX' DSC curves turns from smooth into steep and sharp with rising the heating rate. Similarly,

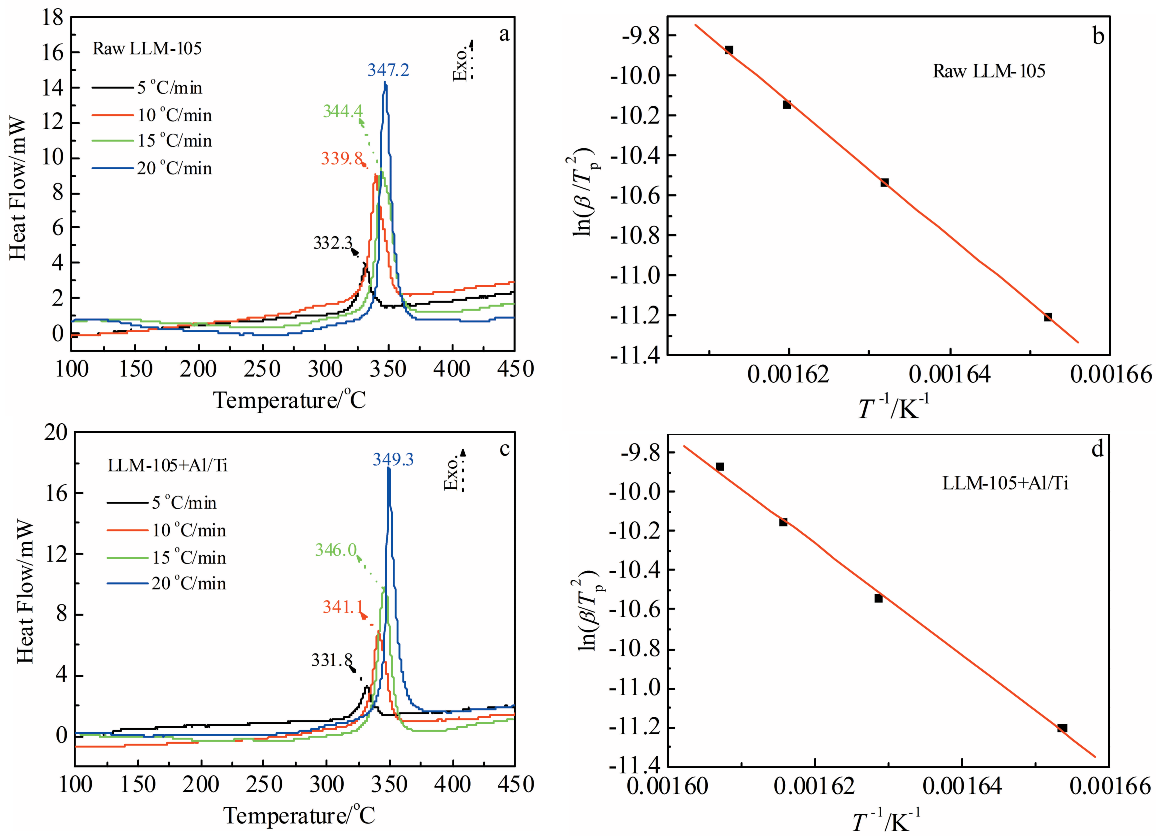

Fig.5 DSC traces of raw LLM-105 (a, b) and LLM-105 doped with Al/Ti composite (c, d)

for the doped RDX with Al/Ti alloy, its melting peaks keep roughly unchanged, and its decomposition peak temperature rises by 21.3 °C from 5 °C/min to 20 °C/min. As a whole, compared with raw RDX, the doped RDX's decomposition peak temperature rises by 0.6, 1.4, 0.6, and 2.6 °C at the same heating rate.

HMX shows the similar pattern with RDX (Fig. 7), i.e., from 5 °C/min to 20 °C/min, the melting peak temperatures of raw HMX and HMX doped with Al/Ti alloy increase by 9.8 and 10.6 °C, respectively. At the same heating rate, the doped HMX has about 1 °C increase in melting peak temperature compared to the raw HMX.

Similarly, CL-20 has the same pattern with the above two explosives (Fig. 8). From 5 °C/min to 20 °C/min, raw CL-20 and the CL-20 doped with Al/Ti alloy have an increasing decomposing peak temperature of 8.8 and 10.2 °C, respectively. At the same heating rate, the doped CL-20's decomposition peak temperature has an increase of 0.8, 0.5, 0.5 °C but a decline of 0.9 °C at the heating rate of 5 °C/min. The explosives' thermodynamic and kinetic parameters are calculated and listed in Table 2.

The three nitroamine explosives will not decompose spontaneously, and their initiation needs some heat to be activated according to the $\Delta H^{\neq}$ values shown in Table 2. In particular, the decline of E_K elucidates the acceleration effect of Al/Ti alloy on the thermal decomposition of the explosives. All positive $\Delta G^{\neq}$ values confirm that the decomposition of nitroamine explosives will not be initiated spontaneously. Meanwhile, a positive value of $\Delta S^{\neq}$ corresponds to an increase in the randomness or disorder of the system when the activation of the molecules occurs. It reveals that the nitroamine explosives' decomposition reaction needs less energy after adding Al/Ti alloy powder. The addition of the alloy powder has also a good promoting effect on the decomposition reaction of nitroamine explosive. This is mainly due to the large specific surface area of the spherical alloy particles. Accordingly, it is

Table 1 Thermodynamic and kinetic parameters

Thermodynamics			Kinetics		
$\Delta H^{\neq}$/kJ·mol^{-1}	$\Delta G^{\neq}$/kJ·mol^{-1}	$\Delta S^{\neq}$/J·mol^{-1}·K^{-1}	E_K/kJ·mol^{-1}	lnA_K	k/s^{-1}
224.195	156.559	108.053	229.4	44.196	1.123
171.858	156.831	24.192	177.022	34.10	0.838
272.653	153.560	192.848	277.787	54.41	1.31
231.078	149.608	131.584	236.226	47.02	3.08

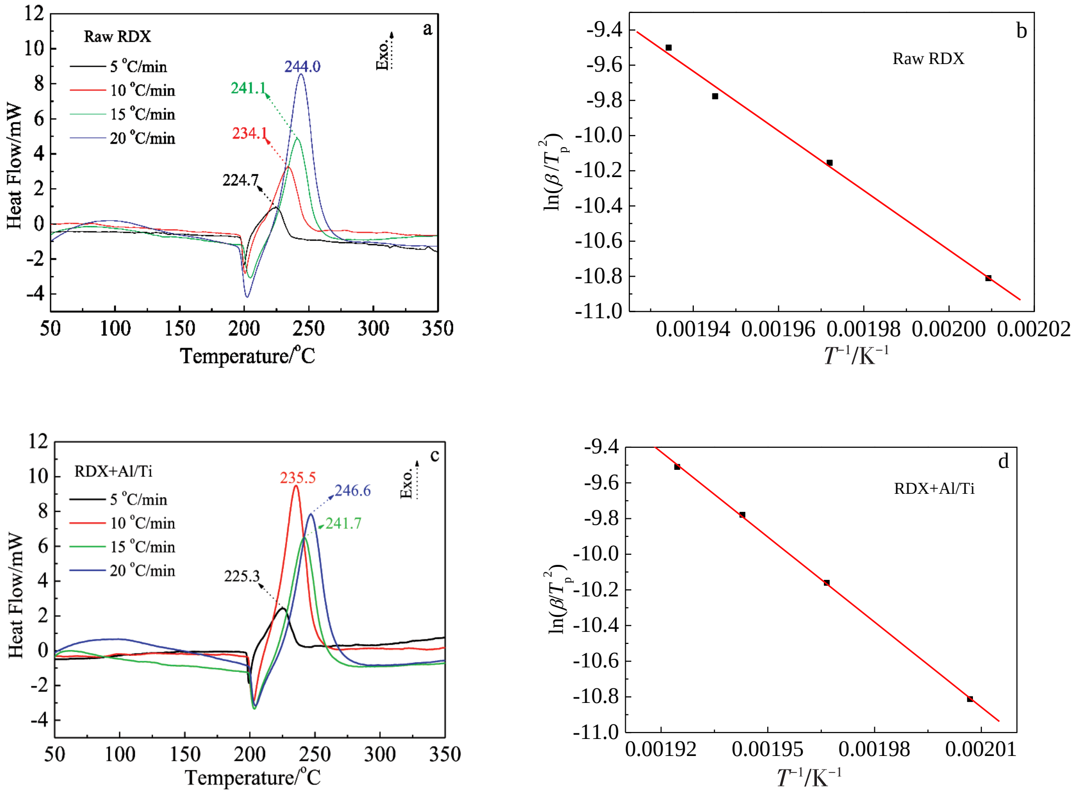

Fig.6 DSC traces of raw RDX (a, b) and RDX doped with Al/Ti composite (c, d)

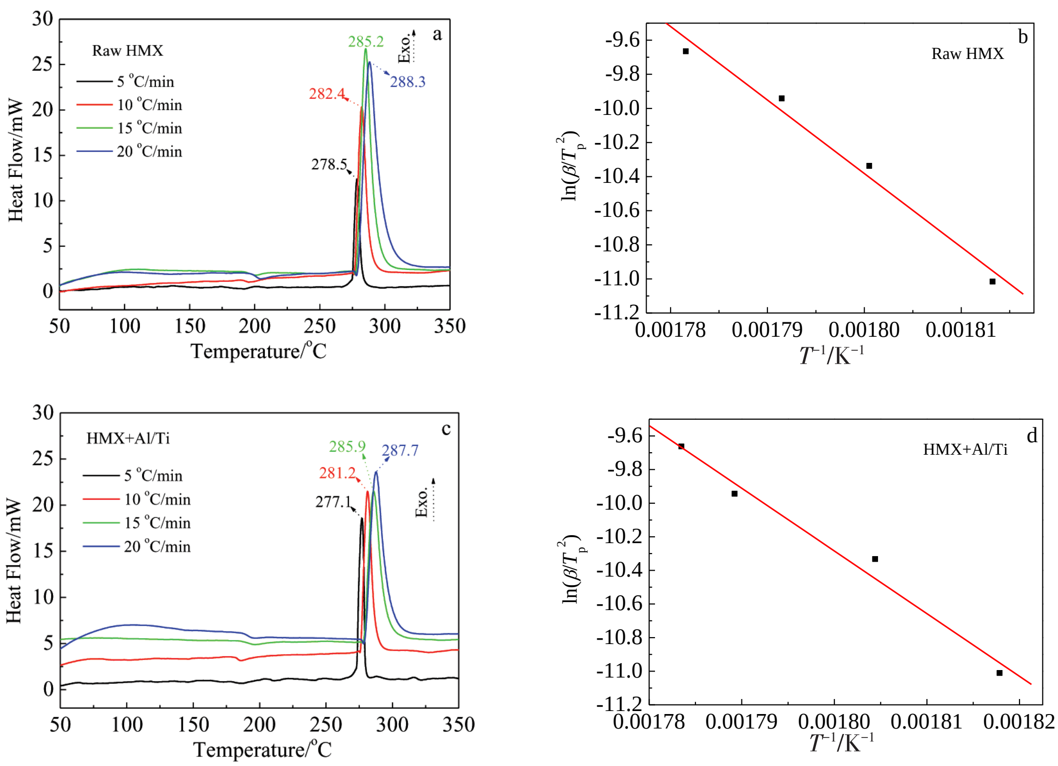

Fig.7 DSC traces of raw HMX (a, b) and HMX doped with Al/Ti composite (c, d)

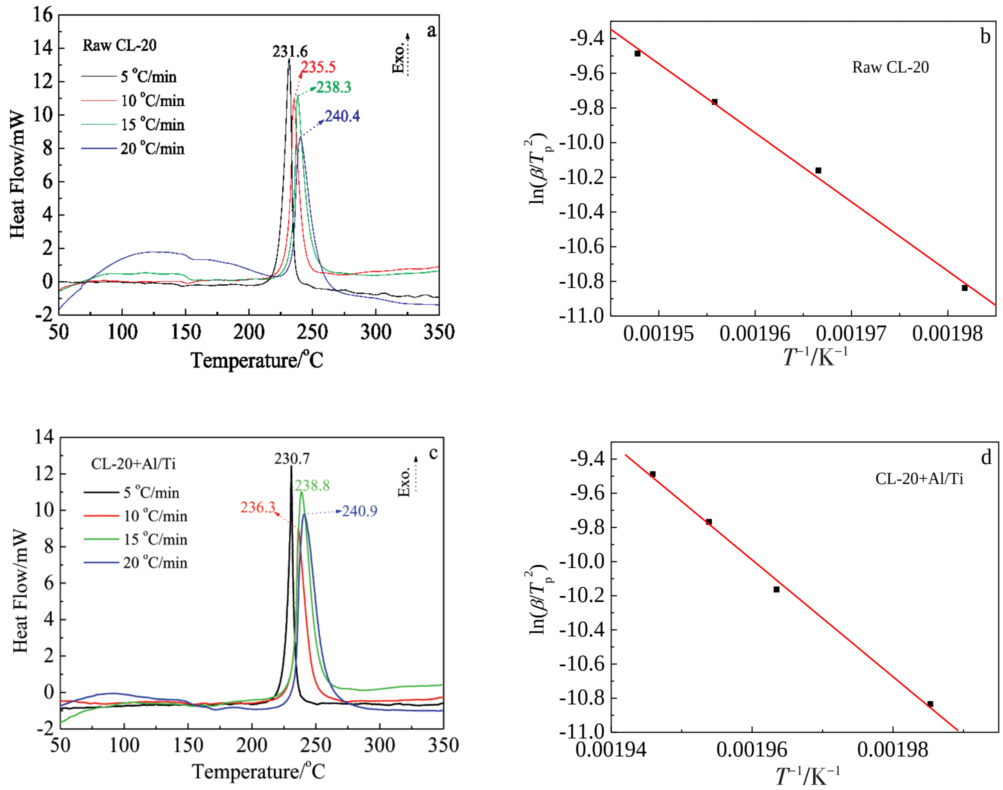

Fig.8 DSC traces of raw CL-20 (a, b) and CL-20 doped with Al/Ti composite (c, d)

Table 2 Thermodynamic and kinetic parameters

Samples	T_p/K	Thermodynamics			Kinetics		
		$\Delta H^{\neq}$/kJ·mol^{-1}	$\Delta G^{\neq}$/kJ·mol^{-1}	$\Delta S^{\neq}$/J·mol^{-1}·K^{-1}	E_K/kJ·mol^{-1}	$\ln A_K$	k/s^{-1}
Raw RDX	514.25	136.597	128.167	16.393	140.872	32.975	1.026
RDX+Al/Ti	514.85	127.962	128.887	12.352	132.242	30.79	0.899
Raw HMX	558.35	353.91	136.51	389.37	358.557	77.92	1.97
HMX+Al/Ti	559.05	305.514	136.781	301.821	310.162	67.39	1.93
Raw CL-20	511.45	326.853	124.000	396.623	331.105	78.71	2.313
CL-20+Al/Ti	511.95	280.99	124.798	303.547	284.455	67.51	1.97

conducive to the heat conduction between the explosive particles and the alloy particles, and is easy to accumulate heat and form hot spots.

3 Conclusions

1) The mechanical mill is employed to prepare the spherical amorphous Al/Ti alloy particles with a mean size of 3.76 μm. The optimum process parameters are thoroughly investigated. It confirms that mechanical mill is a feasible method to prepare spherical amorphous Al/Ti alloy powder.

2) It is ascertained that the spherical amorphous Al/Ti alloy can greatly catalyze the thermal decomposition of five explosives (HNS, LLM-105, RDX, HMX, and CL-20) because the contacting area between the explosive particles and the spherical alloy particles increases.

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非晶态Al/Ti球形金属粒子的制备及其对高能炸药热分解的催化性能

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摘　要：通过控制球磨时间及Al和Ti的质量比，用机械球磨法制备了一种无定型的球形Al/Ti合金粉，其平均粒径为3.76 μm。研究了这种合金粉对HNS、LLM-105、RDX、HMX和CL-20这5种高能炸药热分解的催化作用。结果表明，与原料HNS比较，添加了5%（质量分数）Al/Ti非晶态合金粉的HNS在不同的升温速率下其热分解峰温分别降低了6.9、7.2、4.8和5.2 ℃。同样，对于其它4种炸药，添加Al/Ti后炸药的热分解温度较原料都明显降低。同时，计算了所有炸药样品热分解过程的热动力学参数。结果表明，相对于原料炸药，添加了Al/Ti非晶态合金粉的炸药其热分解活化能分别降低了52.378 kJ·mol^{-1}（HNS）、41.664 kJ·mol^{-1}（LLM-105）、8.6 kJ·mol^{-1}（RDX）、48.4 kJ·mol^{-1}（HMX）和46.7 kJ·mol^{-1}（CL-20）。这说明Al/Ti非晶态合金粉对高能炸药的热分解过程有明显的催化作用。

关键词：球磨；Al/Ti合金粉；催化作用；热分解；高能炸药

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