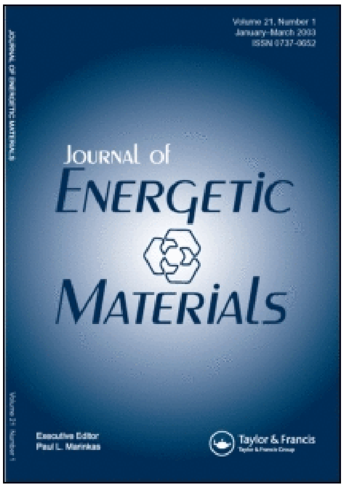

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Thermal Behavior of HMX and Metal Powders of Different Grade

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ABSTRACT

The thermal decomposition characteristic of HMX influenced by the addition of aluminum, nickel, copper with different particle size (general and nano-meter) are studied by PDSC and TG. The results showed that nano copper had the greatest influence on the condensed-phase decomposition characteristic of HMX among the metal powders. Such catalysis effect will be weakened by the decrease of the content of metal powder or the increase of system pressure. Based on the kinetics result inferred from the isothermal DSC experiment, the mechanics of such influence are attributed to the efficacy of catalysis effect, secondary effect and reaction site effect.

INTRODUCTION

When the average diameter of particle is less than 100nm, the particle will possess many interesting properties, such as a large specific area, high reactive ability, etc [1]. Thus, the addition of nano metal powder in propellant will probably be promising due to its high reactive ability. The thrust of this work is to investigate the effect of nano metal powders on the decomposition characteristics of the cyclic nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)—one of the main energetic ingredients used in various propellants and explosives. Understanding the complex physicochemical process that underlie the combustion of such materials can provide a link between the physical properties and molecular structure of these molecules and their combustive behavior, which in turn, may offer some clues for the application of nano metal powder in propellant and explosive to obtain better control of their ignition, combustion, or sensitivity.

EXPERIMENTAL

Thermal Analysis

The work of thermal analysis was performed with a Mettler TA910 Pressure Differential Scanning Calorimeter (PDSC) system and a Mettler TA2950 thermogravimetry. Almost constant sample mass of 0.5 ± 0.1mg placed in encapsulated aluminum pans was used in all experiments. Nitrogen with high purity of 99.99% was used and its flowing rate in the balance and stove of thermogravimetry was 40ml / min and 60ml / min respectively.

Metal Powder Characterization

JSM-5800 SEM made by JEOL Ltd. and Y-4Φ XRD by Dangdong Ray Ltd were used to characterize the metal powders. The various metal powders are approximately spherical

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and the average diameter of metal powders were shown in Table 1. The leader character n- and g- in table1 represent nano and general grade metal respectively.

TABLE 1. Average Diameter of Metal Powder.

n-Al	n-Ni	n-Cu	g-Al	g-Ni	g-Cu
90nm	10nm	90nm	10μm	1.1μm	3μm

Samples Preparation

HMX (technical pure) was sieved by screen cloth of 120 mesh (0.125mm). Mixtures of metal powders and HMX at weight ratios of 3:2 were prepared by careful mixing of the two components in a 5-cm diameter polished porcelain container with a polished glass rod. Ethanol absolute was used as dispersant.

DEFINITIONS

T_l - the temperature at which liquefaction of the condensed phase occurs.
T_o - the (extrapolated) onset temperature at which thermal decomposition or pyrolysis deemed to be underway
T_p - the temperature corresponding to the maximum heat output in the decomposition reaction, as observed in the DSC scan.
$\Delta T = T_P - T_o$
PHC - the Percent of Heat released in the Condensed – phase decomposition; for T_l shown in Table 2 clearly shows that T_l is not influenced by the presence of the metal. It is reasonable to equal PHC to the ratio of the quantity of heat released before 281℃ to the quantity of heat released in the whole range of thermal decomposition.
DTH - the Difference in temperature between T_P for pure HMX and T_P for mixtures of HMX and metal.

RESULTS

DSC Analysis of the Mixtures of HMX and Metal Powders

As shown in Figure 1, three peaks are shown on the DSC curve of pure HMX. The weak endothermic peak (T_m=185℃) is due to the transformation of HMX from the low temperature phase (β) to the high temperature phase (δ)[2]. The sharp endothermic peak at 281.95℃ corresponds to melting. The thermal decomposition commences before the melting process is incomplete ;as a result, the energy released during the onset of the exothermic thermal decomposition swamps that energy taken up by the endothermic melting reaction. The sharp peak (T=286.86℃) immediately after melting is due to the self-decomposition of HMX. On the DSC curve of HMX/n-Cu (3:2, by mass); the decomposition peak of HMX changes from a sharp peak to a gentle slope one and shifted 15.92℃ forward.

Table 2 summarizes the data of DSC parameters recorded for the mixture of HMX and metal powder (3:2,by mass). The results suggest that T_l of HMX remains at 281℃ in all samples and the numerical value of PHC and DTH fluctuated in the same tendency with the different kind of metal, which suggest that PHC can be a rational substitute for DTH to evaluate the effect of metal powder on the condensed-phase decomposition characteristic of HMX. A comparison of PHC among the mixtures of HMX and metal powders shows that n-Cu has the greatest influence on the condensed-phase decomposition of HMX among the nano metal powders (the effect is also shown in Figure 1). Other nano metal powder grades trialled (n-Ni, n-Al) displayed an intermediate effect while the micron grade powders had the least effect (g-Cu > g-Ni, g-Al).

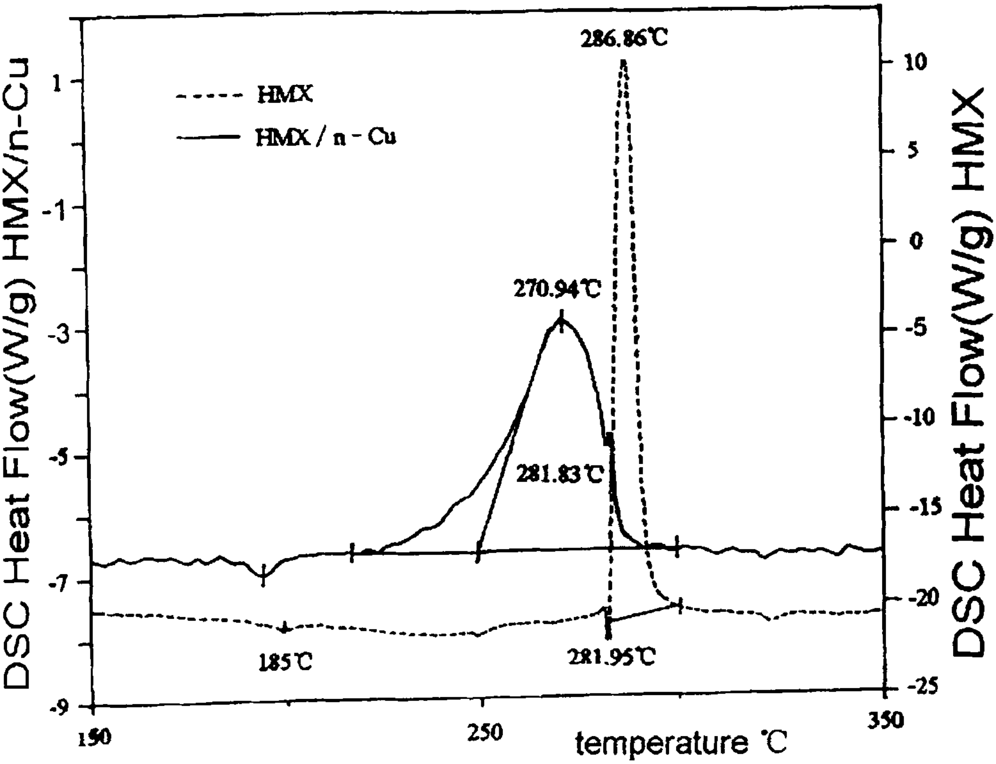

FIGURE 1. DSC Curve of HMX and HMX / n-Cu(0.1MPa; 10℃ / min).

TABLE 2. Description of DSC Traces of HMX and HMX / Metal Powder.
(0.1MPa; 10℃ / min.)

Sample	T_i (℃)	T_O (℃)	T_P (℃)	PHC (%)	DTH (℃)	ΔT (℃)
HMX	281.95	282.48	286.86	1.52	0	4.38
HMX / n-Cu	281.83	249.06	270.94	80.7	15.92	21.88
HMX / n-Ni	281.09	263.69	283.68	38.5	3.18	19.99
HMX / n-Al	281.76	269.04	284.23	35	2.63	15.19
HMX / g-Cu	281.48	281.70	284.73	14.7	2.13	3.03
HMX / g-Ni	280.43	280.80	284.68	9.14	2.18	3.88
HMX / g-Al	281.40	282.14	286.17	2.83	0.69	4.03

The percent and rate of weight loss at different positions – peak onset and maximum respectively—on the TG / DTG curves of HMX / n-Cu(3:2, by mass) are summarized in Table 3. While the DSC peak temperature of HMX / n-Cu is shifted 15.92℃ forward compared with the crystal of HMX, its DTG peak temperature is only 3.67℃ in advance. The cause of this discrepancy lies in the difference of controlling steps between the process of loss of gravity and release of heat. In the condensed-phase decomposition process, the pyrolysis products of HMX may be retained in the solid for long time after they are formed. Their rate of release is substantially controlled by the coalescence of the products and the creation of exit channels from within the particles[3]. Thus the rate controlling steps of loss of gravity will be the relatively slower process compared with the faster process of chemical reaction—the rate controlling steps of release of heat.

As shown in Table 4 and Table 5, T_p (HMX) will increase and PHC will decrease with the decrease of the content of n-Cu or the increase of the system pressure in HMX / n-Cu. That means the catalysis effect will be weakened by the decrease of the content of metal powder or the increase of system pressure.

TABLE 3. Description of the TG /DTG Trace of HMX and HMX / n-Cu.
(0.1MPa; 10℃ / min.)

	Temperature ℃		Percent of Weight loss %		Rate of weight loss % / ℃	
	Onset	Peak	Onset	Peak	Onset	Peak
HMX	281.07	286.79	2.52	31.4	1.618	11.60
HMX / n-Cu	257.46	283.12	8.75	48.25	0.371	1.578

TABLE 4. Description of the DSC Traces of HMX / n-Cu with Different Content of n-Cu.
(0.1MPa; 10℃ / min)

Sample HMX / n-Cu	T_O ℃	T_P ℃	ΔT ℃	PHC %
1:0	282.48	286.86	4.38	1.52
3:2	249.06	270.94	21.88	80.7
2:1	263.65	283.70	20.05	53.2
3:1	265.54	283.82	18.28	41.2
4:1	269.26	285.46	16.20	32.4

TABLE 5. Description of the DSC Traces of HMX / n-Cu at Different Pressure.
(3:2, by mass; 10℃ / min.)

Pressure	Sample	T_o (℃)	T_P (℃)	PHC (%)
0.1MPa	HMX	282.48	286.86	1.52
	HMX / n-Cu	249.06	270.94	80.7
1MPa	HMX	280.37	285.33	0.80
	HMX / n-Cu	277.73	283.01	63.08
5MPa	HMX	277.15	283.10 / 284.60	0.23
	HMX / n-Cu	280.10	282.19	52.5

Kinetic Analysis of HMX/n-Cu

In the decomposition process of HMX, the heating rate is an important parameter in determining what kind of elementary process appears and in what phase the decomposition occurs. As shown in Figure 2, the proportion of condensed phase decomposition of HMX in HMX / n-Cu is declined with the increase of heating rate. The appearance of a sharp self-decomposition peak of HMX indicates that the controlling step of decomposition of HMX is the liquid state decomposition process at or above a heating rate of 20℃ / min. The liquid phase and condensed phase decomposition are based on different mechanism. Our experiment results imply that Kissinger method[4] which is employed for kinetic analysis will not be suitable for analysis the pyrolysis process of HMX / n-Cu at different heating rates we have tried. Therefore, the software package developed by Mettler TA corp. was adopted to infer the decomposition kinetic properties of HMX / n-Cu (3:2, by mass) from the isothermal DSC results in the temperature range of 260℃ to 265℃. The results illustrated in Table 6 show that the decrease in activation energy for the pyrolysis of HMX influenced by n-Cu is 31 KJ / mol. This implies that the energy barrier of pyrolysis of HMX will be decreased by n-Cu, and such decline will lead to the pre-pyrolysis of HMX.

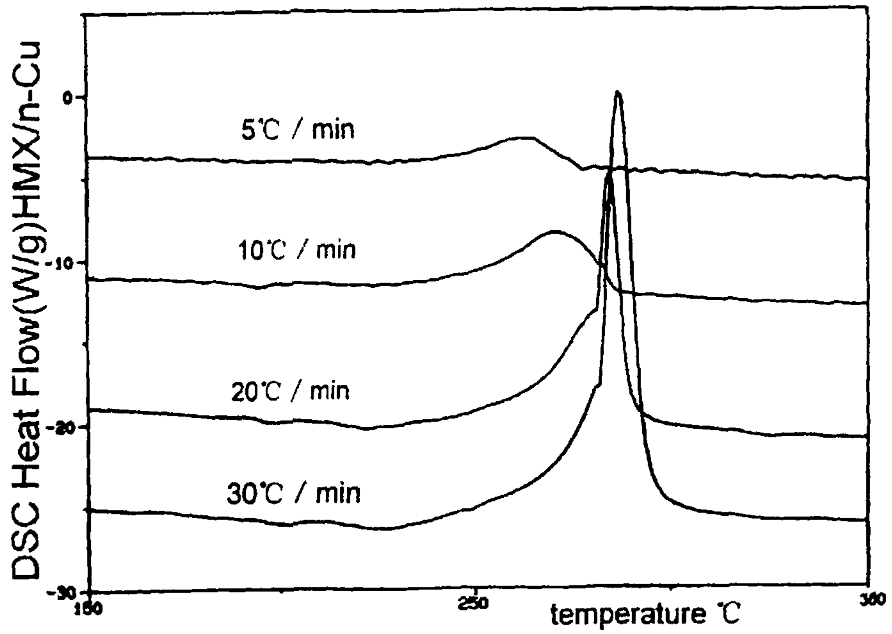

FIGURE 2. DSC Curve of HMX / n-Cu(3:2, by mass) at Different Heating Rate.

TABLE 6. Kinetic Analysis of the DSC Data over Temperature Range 260 - 265℃.

Sample	Activation energy	Log (Frequency factor)
HMX	168±22 KJ / mol	15.5 ± 2.1 min^{-1}
HMX / n-Cu	137±16 KJ / mol	13.1 ± 1.6min^{-1}

DISCUSSION

The present work has revealed the definitive influence of n-Cu on the condensed-phase decomposition properties of HMX. We propose catalysis effect, secondary effect and reaction site effect to describe this process.

The Catalysis Effect of Nano Copper

The complicated condensed-phase decomposition processes of HMX include the unimolecular decomposition of HMX, secondary reactions between HMX and pyrolysis products, and the transportation of the pyrolysis products of HMX. It is well known that copper atoms can react with nitrogen oxide compounds to form complexes and play important catalysis effect in the decomposition of these compounds [5]. The catalysis effect of n-Cu is relative to the unimolecular pyrolysis process of HMX defined as the interaction between n-Cu and the groups of NO_2 in the molecule of HMX. Kung's characterization of the microstructure of n-Cu copper powders using TEM have indicated the existence of annealing twins and triple grain junctions in the grain boundaries of nanocrystalline copper powders [6] .The high reactive ability of atomic copper in the defect of grain boundaries of n-Cu will greatly enhance such interactions and cause the formation of the complex between between n-Cu and the groups of NO_2 in the molecule of HMX. And because breaking of the N-N bond is shown to be the most important step in the unimolecular decomposition of HMX by Quantuchemical calculations [3], the weaken of N-N bond by the catalysis effect of n-Cu will greatly contribute to the decomposition of the HMX molecule.

The Secondary Effect of Nano Copper

The secondary effect of n-Cu is defined as the reduction effect of n-Cu on the pyrolysis products of HMX. The products NO_2 will be involved in the following three reactions to form NO [3,7].

$$NO_2 + CH_2O \rightarrow NO + H_2O + CO \qquad (1)$$

$$NO_2 + H \rightarrow NO + HO \qquad (2)$$

$$2NO_2 \rightarrow 2NO + O_2 \qquad (3)$$

The reduction effect of NO by n-Cu can be described in reaction (4) and (5).

$$4Cu + 2NO \rightarrow 2Cu_2O + N_2 \qquad (4)$$

$$2Cu_2O + 2NO \rightarrow 4CuO + N_2 \qquad (5)$$

According to the principle of thermodynamics, when values of the standard free energy are used, the condition $\Delta_r G_m^0 << 0$ must be taken as the criterion of the feasibility of the process in nonstationary conditions. We get $\Delta_r G_m^0 = \sum_B \nu_B \Delta_f G_m^0(B) = -466.95$ KJ / mol for reaction (4) and $\Delta_r G_m^0 = -401.44$ KJ / mol for reaction (5) using the data in ref [8]. Considerable experimental and Density Functional Calculations also have been performed to understand the reduction mechanisms of reaction (4) and (5)[5,9-11]. In particular, Cu−gem−dinitrosyl species have been suggested to play an important role in N−N bond formation and pyrolysis to N_2 and O_2. The secondary effect of n-Cu will promote the gas-zone pyrolysis of HMX.

The Reaction Sites Effect of Nano Metal Powder

As show in Table 2, the existence of nano metal powder such as n-Cu, n-Ni and n-Al will promote the proportion of condensed-state decomposition of HMX. This phenomenon will be attributed to the consequence of more reaction sites—local heat points and physical adsorption sites—offered by nano metal powders. High coefficient of heat conduction of nano metal powder will lead to the formation of local heat points in the heating process of HMX. Once formed, these hot spots will react exothermically to promote the decomposition of the crystal of HMX. As for the effect of physical adsorption sites, the secondary reactions between the pyrolysis products and the transportation of the pyrolysis products of HMX are taken into consideration. The stability of the HMX crystal lattice will be disrupted by the electrostatic effect in the existence of trapped pyrolysis product such as OH, or the radicals involved in the formation of the amide polymer[12]. Because more pyrolysis products may be trapped by nano metal powders for more physical adsorption sites formed with the decrease of particle size, such effects will lead to the instability of HMX under certain heating conditions.

CONCLUSIONS

By comparison of PHC among the mixtures of HMX and metal powders, we found that nano-copper had the greatest influence on the condensed-phase decomposition process of HMX among the metal powders in our experiments. The extent of such influence will be weakened by the decrease of the content of nano copper or the increase of the system pressure. The mechanics of activation energy of the pyrolysis of HMX decreased by nano-copper are attributed to the efficacy of catalysis effect, secondary effect and reaction sites effect.

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