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Insensitive HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) Nanocrystals Fabricated by High-Yield, Low-Cost Mechanical Milling

Yi WANG[1,2*], Wei JIANG[2], Xiaolan SONG[3], Guodong DENG[2] and Fengsheng LI[*2]

[1]*School of Materials Science and Engineering, North University of China, Taiyuan, China*
[2]*National Special Superfine Powder Engineering Research Center, Nanjing University of Science and Technology, Nanjing, China*
[3]*School of Chemical Engineering and Environment, North University of China, Taiyuan, China*
[*]*E-mail: wangyi528528@aliyun.com*

Abstract: A mechanical approach had been adopted for fabricating HMX nanoparticles. This fabrication method avoided the recrystallization process and was different from the traditional methods employed to prepare nanoexplosives. In particular, the high yield and low cost increased the possibility of its industrial application. Specifically, HMX particles, that had a mean size of 0.27 μm, were prepared by mechanical milling; a significant proportion of nano-HMX (<100 nm) were present and these were observed by TEM and SEM images. The thermal decomposition of HMX samples before and after pulverization was investigated by TG/DSC analysis. The results indicated that there was no obvious difference between the thermographs of raw and pulverized HMX. The HMX samples were investigated by friction, impact, and shock sensitivity tests. High safety was confirmed since pulverized HMX was far more insensitive than raw HMX; indeed the shock sensitivity of pulverized HMX was about 60 percent lower than that of raw HMX.

Keywords: nanoexplosives, HMX, thermal decomposition, sensitivity

Introduction

HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is an excellent explosive with high crystal density (1.902~1.905 $g \cdot cm^{-3}$), high velocity of detonation (about 9110 $m \cdot s^{-1}$ at ρ = 1.89 $g \cdot cm^{-3}$), and high heat of detonation (about 6780 $kJ \cdot kg^{-1}$). However, due to its high sensitivity, HMX is not as safe to use as TNT. The long distance of sympathetic detonation is a particular hazard for soldiers. Because of this, much research has been done to reduce the sensitivity of high explosives. The most common method used is surface coating, *i.e.* decreasing the sensitivity of HMX (or RDX) particles by coating their surface with inert materials [1, 2]. However this method is no longer recommended since the performance may be impaired by the introduction of inert materials. Many studies have reported that the sensitivity of high explosives would be changed if their crystal properties were changed [3, 4]. To clarify this situation we introduced the fractal approach to quantifying the crystal properties of nitramine explosives and to assessing their risks [5-7]. This approach bridged the gap between the properties of crystals and their sensitivity, and these results further confirmed the existence of the relationship. However, for micron sized explosives, the changes in sensitivity that derived from the changes in crystal properties were insufficient to ensure the high safety of the explosives. Hence, our study will disclose to what extent the sensitivity was changed when the size of the explosive particles was reduced to the nanometer scale.

Various nanoexplosives have been prepared by different methods [8-13]. Most of the fabrication processes were achieved by a common mechanism, recrystallization (a short-time process). Here we will not discuss the advantages and disadvantages of the recrystallization method for the preparation of nanometer (or submicron) explosives, but rather initiate another approach for the fabrication of nanometer (or submicron) explosives, *i.e.* comminution of coarse particles to nanometer (or submicron) particles. The former methods that are based on recrystallization relate to crystal growth and the latter concerns crystal breaking. So many theories about recrystallization have been developed, but few researches have concerned mechanical methods. In fact, since it is a lengthy process, particle smashing is as elaborate as particle growth. This study constitutes a preliminary investigation, in which the fabrication, micron morphology, thermolytic characteristics, and safety of pulverized HMX (nanocrystals) will be introduced.

Experimental

Sample preparation

The raw HMX was pulverized by an improved, bi-directional, superfine milling process designed by Prof. Fengsheng Li [14]. In this device, the cavity wall and the axis can be rapidly rotated in opposite directions. Cooled water can be circulated through the rotating shell and the axis. About 180 grams of raw HMX were crushed per batch, and milling duration, solids loading, medium formulation, and rotation speeds were held constant. Of these factors, the medium is very important. Not less than 30 wt% deionized water was present in the medium to ensure the safety of the fabrication. Other organic liquids which were present were two alcohols (reported in [15, 16]) that served as surfactants to improve the particles dispersivity. In fact, which organic liquids are used is not important. They are used to make the HMX particles well dispersed. There are many organic liquids that can be used as long as they cannot dissolve HMX and are readily miscible with water.

Sample characterization and tests

The particle size and size distribution were measured with a laser particle sizer, Master Sizer Instrument. The morphology was observed with an optical microscope (Nikon eclipse 55i), a transmission electron microscope (TEM, JEOL JEM-200CX), and an S-4800 field-emission scanning electron microscope (SEM, Hitachi, S4800). The phases of the samples were investigated with an X-ray diffractometer (XRD, Bruker Advance D8), using Cu K_α radiation at 40 kV and 30 mA. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on a TA Model Q600 TG/DSC simultaneous thermal analyzer.

The impact sensitivity of the samples was tested with an HGZ-1 impact instrument. The special height (H_{50}) represents the height from which a 2 kg (or 5 kg) drop-hammer will result in an explosive event in 50% of the trials. In each determination, 25 drop tests were made in order to calculate the H_{50} and each lot was tested three times to obtain a mean value ($\overline{H}_{50}$) and a standard deviation ($S_{dev.}$). The friction sensitivity of the samples was tested with a WM-1 friction instrument, and three test standards were adopted (66 ±1°, 2.45 MPa; 80 ±1°, 2.45 MPa; 90 ±1°, 3.92 MPa). In each determination, 50 samples were tested and an explosion probability (P, %) was obtained. Each lot was tested three times to obtain a mean value ($\overline{P}$) and a standard deviation ($S_{dev.}$).

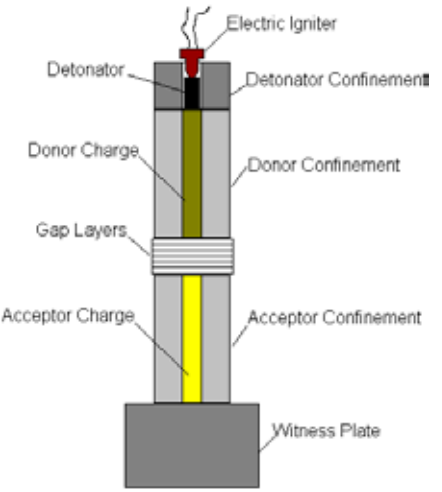

Figure 1. Schematic profile of the device for the small scale gap test.

Table 1. Characteristics and dimensions of the components for the small scale gap test

Component	Characteristics	Dimensions
Electric igniter	self-prepared	-
Detonator	# 30 flame detonator	-
Detonator confinement	# 45 steel	Ø 25 mm × 16 mm
Donor charge	refined RDX from acetone	Ø 5.1 mm × 38.15 mm
Donor confinement	# 45 steel	Ø 25 mm × 38.15 mm
Gap layers	PMMA	Ø 25 mm
Acceptor charge	explosive samples	Ø 5.1 mm × 38.15 mm
Acceptor confinement	# 45 steel	Ø 25 mm × 38.15 mm
Witness plate	# 20 mild steel	Ø 40 mm × 20 mm

The shock sensitivity was examined by the small scale gap test (SSGT). In SSGT, the standard of GJB2178.1A-2005 was adopted (Test methods of safety for booster explosive. Part I: Method of Small Scale Gap Test). Figure 1 shows schematically the components for the SSGT tests, the characteristics and dimensions of which are listed in Table 1. The density of the donor charge (RDX) was 1.48 ±0.01 g·cm^{-3}. The acceptor charge was loaded at a density of 90% TMD. The half depth of the dent obtained at a detonation event with no gap between the donor charge and acceptor charge was used as the limiting value. If the witness depth was deeper than the limiting value, this was judged

to be an explosive event and this gap thickness was assumed to be adequate. For each sample, the range of adequate gap thicknesses (T_{SSGT}) was given. No binder was used in all SSGT tests.

Results and Discussion

Particle size, morphology and structure

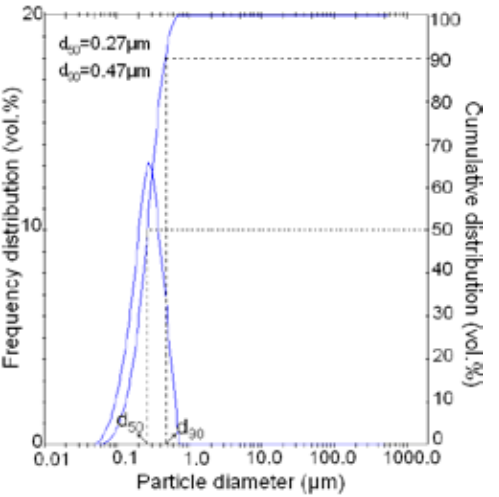

Figure 2. Particle size distribution of the pulverized HMX.

The size and size distribution profiles of the pulverized sample are shown in Figure 2. The particles show a rather narrow size distribution, most of which have sizes less than 0.47 μm (d_{90}). This result indicated that not all of the pulverized HMX particles have their diameter less than 100 nm. Three reasons may account for this result. One is the resolution of the particle size instrument (>0.05 μm); the second is the agglomeration of particles; thirdly, some of particles actually had sizes greater than 100 nm. TEM and SEM analyses were used to probe the morphology of the micron sized particles and to address the question as to whether the pulverized HMX contained nanoparticles. The TEM image in Figure 3 confirms the existence of nanoparticles (<100 nm). The bubbles in Figure 3b imply that the pulverized HMX may decompose under an electron beam of 200 keV. This phenomenon can be mitigated by decreasing the accelerating voltage or by freezing the samples. In the SEM images (Figure 4), a large number of nanoparticles was also observed, and furthermore most of the larger particles

(>100 nm) show diameters of less than 300 nm. In addition, the HMX particles showed a spheroidal shape after milling, which may explain their higher safety. In addition to the particle size and morphology, the crystal phase of the HMX was also examined. The XRD patterns in Figure 5 revealed that the phase of the pulverized HMX was the same as that of the raw HMX (β-HMX, PDF#42-1768).

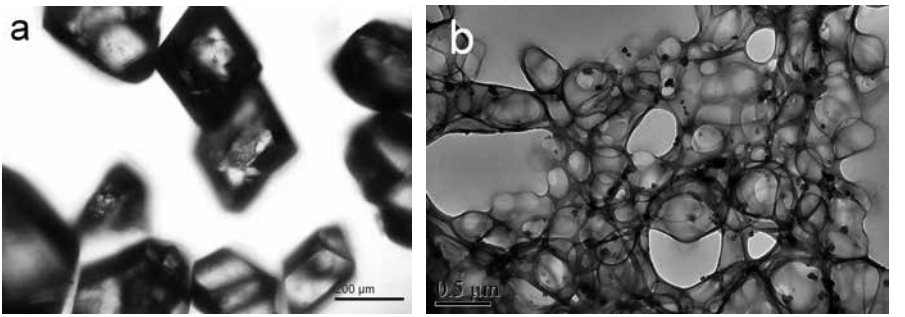

Figure 3. Micron morphology of the samples: (a) optical micrograph of raw HMX; (b) TEM image of pulverized HMX.

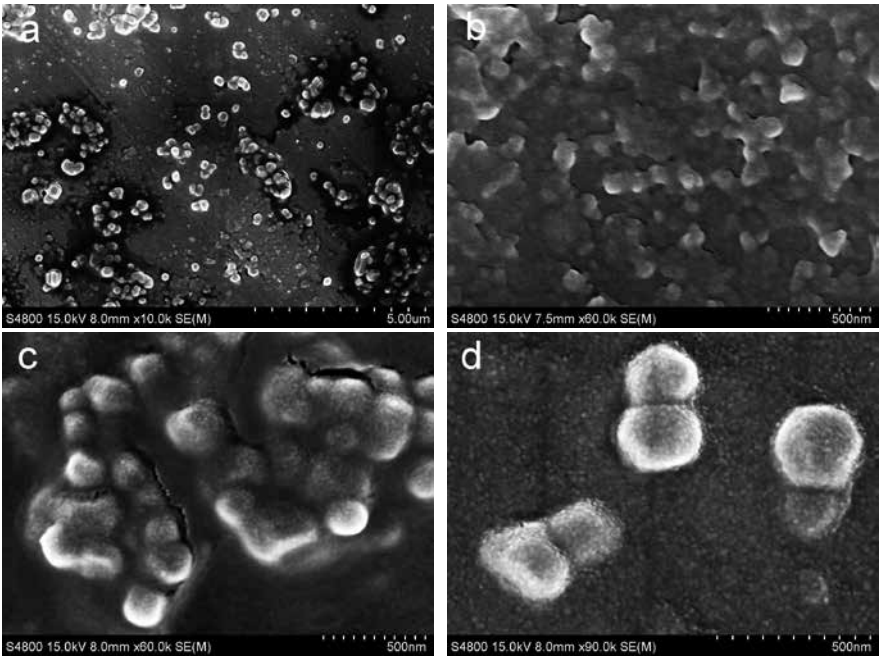

Figure 4. SEM images of pulverized HMX; (b-d) are images of the particles shown in (a) at higher magnification.

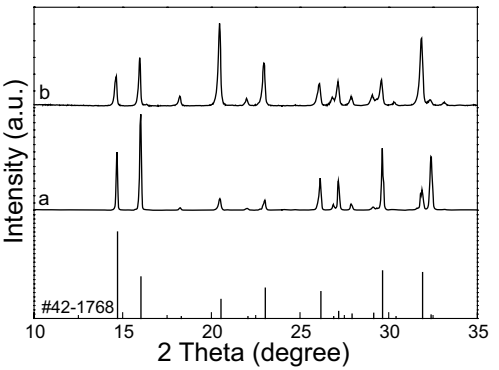

Figure 5. XRD pattern of HMX samples: (a) raw HMX; (b) pulverized HMX.

Thermal analysis

The thermolytic behaviour is an important property in the evaluation of the thermal stability of energetic materials. For composites such as aluminum fueled formulations, the ignition temperature decreased remarkably and the burning rates increased considerably when nano aluminum replaced the micro aluminum as the fuel [17, 18]. For monomolecular energetic oxidizers such as ammonium perchlorate, its thermal decomposition is very dependent on particle size [13]. Decreased thermal stability becomes an important factor that decreases the insensitivity of energetic materials. In the present work thermal analyses of HMX samples before and after pulverization were performed and the results are presented in Figure 6 and Table 2. This indicated that the thermal decomposition of pulverized HMX coincides almost exactly to the decomposition of raw HMX. Specifically, T_P (peak temperature) for pulverized HMX is 2.6 °C lower than T_P for raw HMX; ΔH (heat of decomposition) for pulverized HMX is slightly higher than ΔH for raw HMX. The DTG curves were derived from TG traces, and the value of $|dm/dT|$ (as a function of temperature) was proportional to the rate of decomposition. The value of $|dm/dT|$ indicates the weight decrease of the sample per unit increase in temperature. The $|dm/dT|_{max}$ (maximum value) for pulverized HMX is clearly larger than the $|dm/dT|_{max}$ of raw HMX, and the size decrease (*i.e.* specific surface area increase) may account for this.

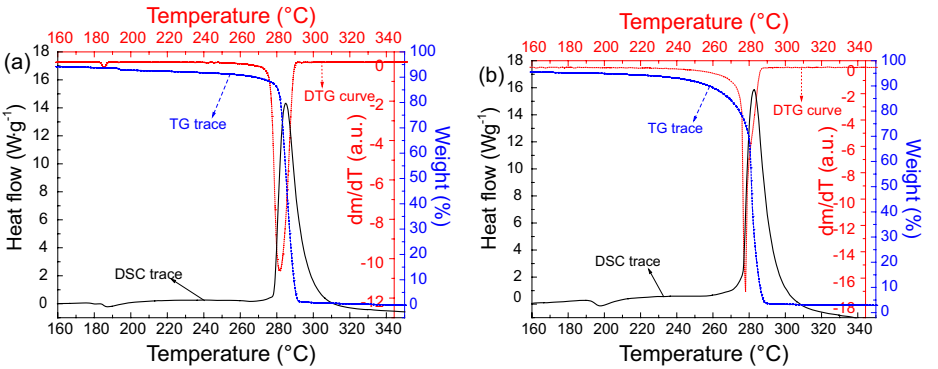

Figure 6. TG/DSC/DTG traces of HMX samples: (a) raw HMX; (b) pulverized HMX.

Table 2. Thermal analysis results for raw and pulverized HMX

Sample	T_p [°C]	ΔH [J·g^{-1}]	$\lvert dm/dT \rvert_{max}$
Raw HMX	284.9	1043	10.7
Pulverized HMX	282.3	1095	17.0

Safety evaluation

In the present study, the main aim in fabricating nano-HMX was to enhance its insensitivity. The mechanical and shock sensitivities of milled samples were tested practically and the results are shown in Tables 3 and 4. In addition, raw HMX and regular RDX were also tested under the same conditions for comparison. The impact sensitivity of pulverized HMX was lower than that of raw HMX; in fact there was almost no explosion event in the test using a 2 kg hammer. The friction sensitivity of pulverized HMX was also lower; however, as the load was increased, the difference between samples became less clear. For the SSGT tests, the difference in shock sensitivity demonstrated that pulverized HMX is a high explosive with insensitive characteristics. The shock sensitivity of the raw HMX and regular RDX (listed in Table 3) were consistent with data reported elsewhere, but the shock sensitivity of pulverized HMX was lower than that of RS-HMX (or RS-RDX) which were obtained by optimizing their crystal properties [19-21]. Therefore, for nitramines, fabricating the nanoexplosives by pulverization may be a better method for improving their safety.

Table 3. Impact and shock sensitivity of samples

Sample	Impact sensitivity				Shock sensitivity
	2 kg hammer		5 kg hammer		range of adequate gap thickness [mm]
	$\overline{H}_{50}$ (cm)	$S_{dev.}$	$\overline{H}_{50}$ (cm)	$S_{dev.}$	
Raw HMX	32.6	3.7	11.4	2.2	12.36~12.96
Pulverized HMX	>79.4	-	27.6	5.2	4.58~5.54
Regular RDX	46.1	4.8	15.3	1.2	13.82~14.42

Table 4. Friction sensitivity of samples

Sample	66°, 2.45MPa		80°, 2.45MPa		90°, 3.92MPa	
	$\overline{P}$ [%]	$S_{dev.}$	$\overline{P}$ [%]	$S_{dev.}$	$\overline{P}$ [%]	$S_{dev.}$
Raw HMX	70.0	5.3	87.3	6.1	98.7	2.3
Pulverized HMX	46.0	2.0	66.0	3.5	96.7	2.3
Regular RDX	68.7	1.2	74.0	6.0	97.3	3.1

Conclusions

HMX nanocrystals were fabricated using a horizontal ball mill. The pulverized samples showed narrow size distributions, had calculated sizes of 0.27 μm (d_{50}) and 0.47 μm (d_{90}). HMX nanoparticles (<100 nm) were observed in the TEM and SEM images. Thermal analysis confirmed that there was no distinct difference in thermal decomposition between the raw and the pulverized HMX samples. Their safety was evaluated by testing their impact, friction, and shock sensitivities. These results indicated that the three types of sensitivity of HMX obviously decreased when the coarse particles were comminuted into nanocrystals; this was especially marked for the shock sensitivity which was reduced by about 60 percent. These results imply that this pulverized HMX may be used as a type of Insensitive High Explosive.

Acknowledgement

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