Full Paper

Synthesis and Desensitization of Nano-β-HMX

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Abstract: Efforts are made worldwide to desensitize explosives against accidental initiation. For several years, nanostructuring of explosives is a promising field of research aiming for this goal. In this work we describe the continuous preparation of nano-β-HMX and a promising approach towards the desensitization of nano-energetic materials. By means of the Spray Flash-Evaporation (SFE) technique, nano explosives and nano composites with reproducible properties can be prepared in a single processing step. By increasing the thermal effusivity of an energetic nanomaterial the heat created by hot-spots can more rapidly be dissipated, reducing the risk of an unwanted reaction.

Keywords: Spray flash-evaporation · nano-HMX · Energetic nanomaterials · Thermal effusivity

1 Introduction

HMX (cyclotetramethylenetetranitramine), which belongs to the class of energetic nitramines, is a well known explosive that is obtained as a by product in the RDX synthesis. With a detonation velocity of $9100 \, \mathrm{m \, s^{-1}}$ at a density of $1.96 \, \mathrm{g \, cm^{-3}}$ a considerable performance gain can be achieved replacing RDX by β-HMX [1].

In view of the continuous improvement of military equipment, the operator's safety gets more and more into the research focus. The accidental initiation of explosives is the consequence of the interplay of heat releasing and heat dissipating processes. A key role in the accidental ignition chain is the conversion of unintentionally applied energy into heat, taking place in local spots, in general called 'hot-spots'. Hot-spots are preferentially formed at heterogeneities within the energetic material, such as voids, crystal defects, gaseous inclusions or impurities. The basic conversion processes taking place at those heterogeneities can be summed up to [2, 3]:

(a) Adiabatic compression of gaseous inclusions, cavities and voids;
(b) Viscous and plastic deformation;
(c) Frictional heating;
(d) Inter-crystalline shearing;
(e) Spark discharge.

Depending on their particular position, inside or outside of the explosive particle, hot-spots are classified into internal and external hot-spots [4]. By aiming for the elimination of hot-spots, two basic approaches to desensitize explosives emerged over the past years: First, reducing the size and number of intercrystalline defects, unwanted inclusions or voids by a slow and controlled recrystallization of the explosive or second by decreasing the particle size of the explosive thus far that the formation of intercrystalline heterogeneities is unlikely to appear [5–12].

According to Tarver, the critical temperature for a 2 µm sized hot-spot in HMX must reach 985 K to initiate the energetic material, whereas a 0.2 µm sized hot-spot must reach the critical temperature of 1162 K [13]. Therefore, a submicrometer- or nanosized HMX with consequently smaller hot-spots should be less sensitive towards initiation than the classical micrometer-sized HMX.

Following the second approach by using the Spray Flash-Evaporation (SFE) process, various energetic materials can be nanocrystallized in large quantities [14]. The SFE process takes advantage of the pressure dependence of the boiling temperature of liquids. A low boiling solvent-explosive solution is set under pressure and heated above its normal boiling temperature. By depressurizing the superheated solution, the excess thermal energy converts into latent energy, causing the instantaneous evaporation of the solvent. As the process uses common solvents such as acetone, methyl *tert*-butyl ether, ethyl acetate or mixtures of those, high production capacities of several grams per hour can be achieved. The median particle size that can be obtained by this process ranges from 50 to 500 nm.

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2 Results and Discussion

2.1 Preparation of Nano-β-HMX

Depending on the crystallization conditions HMX may form four stable polymorphs at room temperature, designated as α-, β-, δ- and γ-HMX. From the military point of view only the β-polymorph is of interest as it combines the highest density, impact sensitivity and detonation velocity of all HMX polymorphs. According to Matzger and Landenberger, the densities of the individual polymorphs decrease in the order β ($1.903\,g\,cm^{-3}$) > α ($1.839\,g\,cm^{-3}$) > γ ($1.78\,g\,cm^{-3}$) > δ ($1.759\,g\,cm^{-3}$) [15]. According to Lee et al. the β-polymorph is preferably formed by recrystallizing HMX from acetone [16].

In this work, nanostructured HMX was prepared by means of the SFE technique where an acetone-HMX solution is superheated above its normal boiling temperature and subsequently atomized into a vacuum chamber (Figure 1). The acetone-HMX solution was prepared by dissolving class 5 HMX (7.9 g, purity >98.8%) in acetone (500 mL, HPLC quality >99.8%, Sigma Aldrich). Using compressed nitrogen, the solution was subsequently pressurized to 6 MPa and atomized by a 60 μm hollow cone nozzle into a vacuum chamber. The pressure in the vacuum chamber was kept constant at about 500 Pa using a DUO Balzers vacuum pump with a $35\,m^3\,h^{-1}$ flow rate. Heating of the solution happens just before the atomization. The nozzle was heated to 160 °C, keeping the thermal load onto the dissolved explosive as low as possible. The strong temperature drop accompanying the evaporation has a protective effect on the sensitive nanoparticles. Separation of the nanoparticles happens by means of parallel arranged axial cyclones, allowing a continuous operation of the process. As the axial cyclones are operated in the vacuum, the cut-off diameter of the cyclones considerably decreases, enabling the separation of nanoparticles from the gas flow [17–20].

In total, 3.43 g HMX was collected by the cyclones in 56 min, resulting in a yield of 43.4%. The low yield is the consequence of a too narrow atomization chamber where to a large extent nanocrystallized HMX deposited. Gravimetric analyses indicated that less than 5% of the total amount of HMX passed the cyclones. Particles that were passing the cyclones are separated in the oil of the vacuum pump so that during operation a release of nanoparticles to the environement can be neglected. Due to the accumulation of nanoparticles with time, a more frequent oil change must be taken into consideration for safety reasons.

2.2 Preparation of a Nano-β-HMX/Licowax Composite

In the same manner as the pure HMX the preparation of a 1% HMX/wax composite was carried out. Class 5 HMX (7.88 g) and Clariant Licowax BJ (81 mg) were dissolved in acetone (500 mL) with the help of ultrasound and slight heating. Afterwards, the solution was atomized at similar process conditions as described before. According to the manufacturer, Licowax BJ is an ester wax with beeswax like properties and a drop point temperature of about 74 °C. In total 5.15 g of the HMX/Licowax composite was collected within 52 min of operation, resulting in a yield of 64.7%.

2.3 Raman Spectroscopy

The formation of the β-polymorph in both nanocrystallized samples could be proven by Raman spectroscopy (Figure 2). β-HMX has a unique band sequence in the region $1150–1400\,cm^{-1}$, which was used for its identification. Although Licowax has a distinctive Raman spectrum as well, the characteristic bands were not found in the HMX/Licowax sample. The Licowax content in the sample is too small to distinguish from the baseline noise.

2.4 Particle Size and Morphology

A scanning electron microscopy image (SEM) of the raw HMX used in this work is depicted in Figure 3. Due to their larger size, the micrometer-sized particles are more stable as they better dissipate the energy from the focussed electron beam.

From experiments with other types of nanostructured explosives, it could be observed that nanoexplosives rapidly melt or even decompose when exposed to the focussed electron beam under high vacuum. In order to prevent any alteration of the morphology, the samples had to be ana-
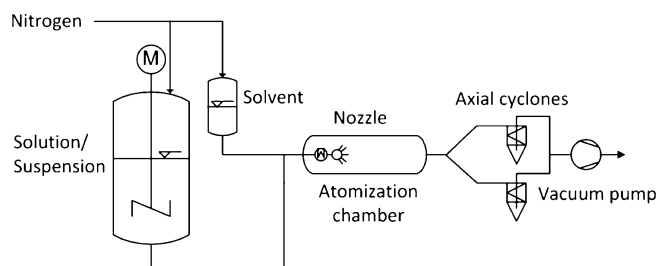

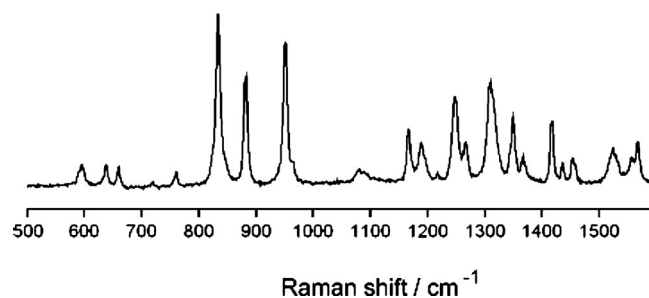**Figure 1.** Spray Flash-Evaporation process flow chart.
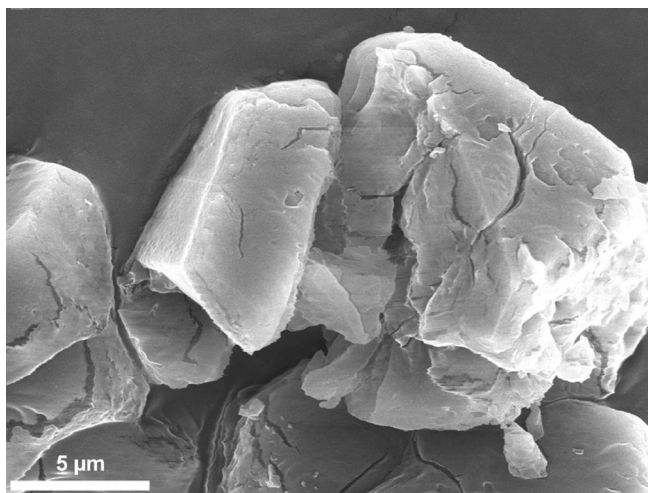

Figure 2. Raman spectrum of nano-β-HMX.

Figure 3. SEM image of micrometer-sized raw HMX.

Figure 5. Particle size distribution of nano-β-HMX.

lyzed at ambient conditions using atomic force microscopy (AFM).

Prior analysis, pellets of 4 mm diameter and about 2 mm height were pressed with a pressure of 100 MPa. Using double sided adhesive tape, these pellets were attached to a metallic support disc for further processing. Subsequently, about 200 μm from the pellet surface were gradually scraped of by means of a Leica RM 2145 microtome. The last cutting steps were performed at the smallest cutting depth of 1 μm. By means of this technique a median surface roughness of about ± 100 nm was achieved.

A 5×5 μm AFM image of the pressed and cut nano-β-HMX pellet is depicted below (Figure 4).

By measuring 200 individual particles an accurate particle size distribution was obtained (Figure 5). The median parti-
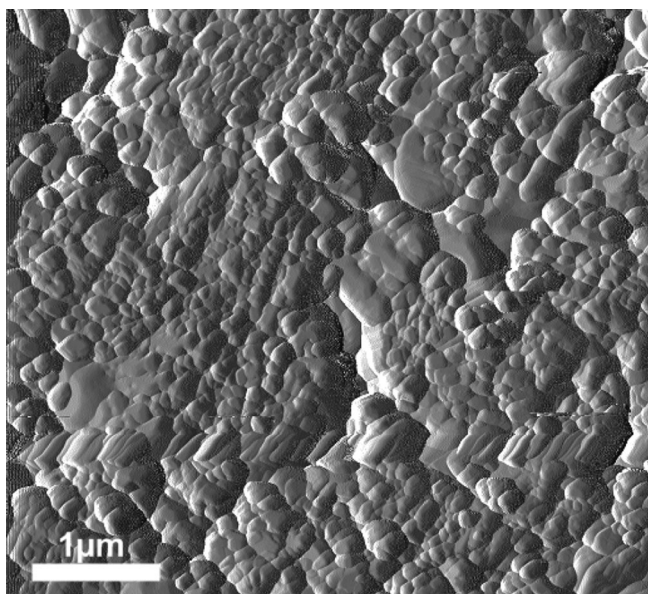

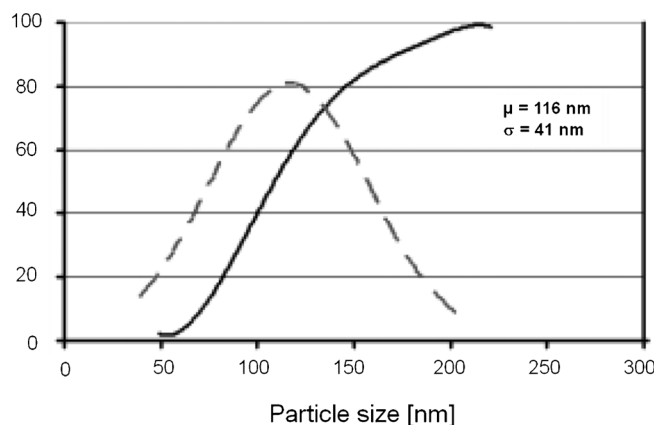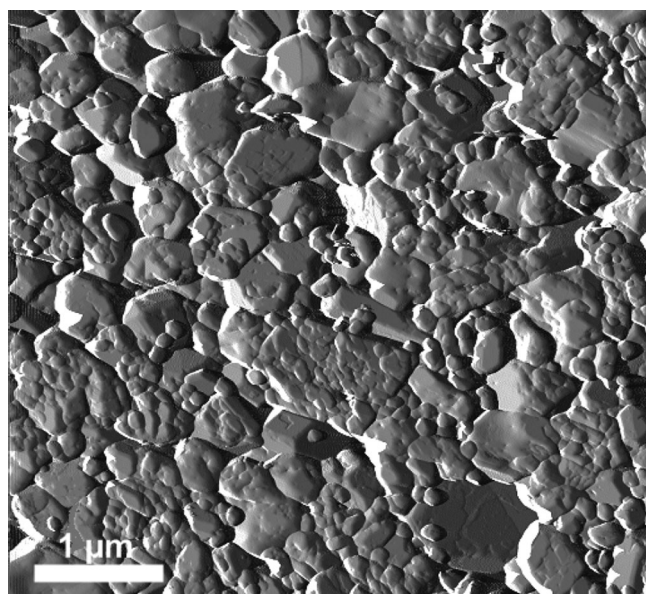**Figure 6.** AFM image of the pressed nano-β-HMX/Licowax composite.

cle size μ in this sample is 116 nm with a variance σ of 41 nm.

The addition of a second compound to the explosive solution can have a significant influence on the particle properties as found out earlier [14]. In this case, the addition of 1% Licowax to the HMX-acetone solution promoted the formation of larger particles (Figure 6). A remarkable amount of particles in between 400 to 600 nm were found in the 5×5 μm AFM image shown below.

With increasing particle diameter, a considerable broadening of the particle size distribution could be observed as well (Figure 7).

For reasons of clarity, the same scales were used for both particle size distributions. Although the median particle diameter μ in the HMX/Licowax sample only slightly in-
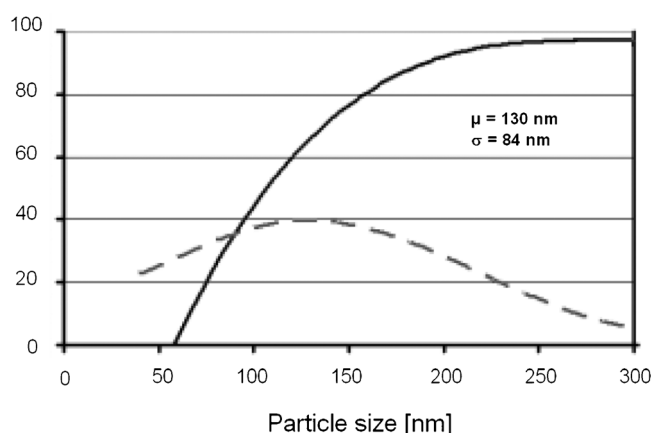

Figure 4. AFM image of pressed nano-β-HMX.

Figure 7. Particle size distribution of nano-β-HMX/Licowax.

creased to 130 nm, the variance σ spread to 84 nm. It is assumed that the higher yield of collected material is the consequence of the larger and heavier particles, being better separated by the cyclones.

2.5 Sensitivity

According to the BAM (Bundesanstalt für Materialprüfung) guidelines the sensitivity towards initiation by impact, friction and electrostatic discharge (ESD) was measured (Table 1).

Table 1. Sensitivity towards impact, friction and ESD of the micrometer- and nanosized HMX samples.

Formulation	Impact [J]	Friction [Nm]	ESD [mJ]
micro-β-HMX	> 6.5	>120	280.57
nano-β-HMX	> 1.5	>168	374.09
nano-β-HMX/Licowax	> 2.0	>192	419.83

In contrast to the expected desensitization, a considerable increase of the impact sensitivity could be observed for nano-HMX. As proposed by Zygmunt, hot-spots can be classified as internal and external hot-spots according to their particular position [4]. By decreasing the particle size the formation of internal defects, acting as hot-spots, is less likely. However, at the nanoscale it is assumed that interparticle voids may behave as external hot-spots. Due to the homogeneous distribution of the interparticle voids, multiple external hot-spots can be simultaneously formed upon impact, considerably lowering the impact sensitivity.

2.6 Thermal Effusivity

The term thermal effusivity describes the ability of a given material how fast it can exchange heat with its environment. The thermal effusivity *e* is formed as follows:

$$e = (k \times \rho \times c_p)^{0.5}$$

with *k* the thermal conductivity, ρ the density and c_p the specific heat capacity. The unit of the thermal effusivity *e* is [Ws$^{1/2}$ m^{-2} K^{-1}].

Considering a hot-spot as 'environment' the importance of the thermal effusivity becomes obvious, as the speed with which the heat from the hot-spot dissipates decides if a chain reaction sets in or not.

In the case of nano explosives where the interparticle voids are generally filled with air, thermal effusion is hindered. By filling these voids with an inert and heat conducting material the formation of hot-spots is hindered and heat dissipation can be improved.

The thermal effusivity of nanostructured and micrometer-sized HMX was measured using a TCi C–Therm thermal conductivity analyzer (Table 2). As the nanopowder must be in a close contact with the sensor surface, pellets with

Table 2. Comparison of the thermal effusivity of the different types of HMX and pure Licowax BJ.

Formulation	Thermal effusivity [Ws$^{1/2}$ m^{-2} K^{-1}]
Licowax BJ	606.4
micro-β-HMX	181.5
nano-β-HMX	244.3
nano-β-HMX/Licowax 99/1	403.1

15.8 mm diameter and about 5 mm height were pressed at a pressure of 22.3 MPa. From the pure Licowax a pellet of the same height was prepared by melting approximately 3 g of the raw material and pouring it into a round mould where it was allowed to solidify. For a better contact between the sample and the sensor a 500 g weight was placed on the pellets during the measurement.

Due to the larger grain size, micrometer-sized HMX can not be pressed into stable pellets without any binder. Therefore, the thermal effusivity had to be measured from the loose powder. For this purpose, a mould was placed on the sensor where a defined volume (1.25 mL) of the loose powder was filled into it.

As can be seen from Table 2, the thermal effusivity of nanosized HMX considerably increased through the addition of Licowax. If the increase of thermal effusivity is directly related to the implementation of nanosized Licowax droplets into the interparticle spaces can not be said for sure at the moment. As the addition of Licowax to the HMX solution caused spreading of the particle size distribution, filling of interparticle voids by larger and smaller HMX particles must also be taken into consideration.

As the thermal effusivity of micrometer-sized HMX was measured from the loose powder, the entrapped air falsifies the measured values. For this reason the values for micrometer-sized HMX can not be compared directly with those of the pressed nano powders.

We assume that filling of interparticle voids with a highly thermal conducting material, preferably a nanomaterial fitting exactly into the void, a considerable decrease of the impact sensitivity should be obtained.

3 Conclusion

In this work the formation of nano-β-HMX and its desensitization by increasing its thermal effusivity are described. Using a Spray Flash-Evaporation process, multiple grams of nano- and submicrometer-sized HMX were prepared, having a median particle size of around 116 nm. The formation of the β-polymorph was confirmed by its Raman spectra. The impact sensitivity of nano-β-HMX is considerably lower than those of micrometer-sized β-HMX. As a consequence of the nanostructuring process it is assumed that interparticle voids are acting as external hot-spots, making the explosive more sensitive to impact than before. However, the relocation of the hot-spots to the particle outside makes them easier accessible for elimination. The addition of a small amount of Clariant Licowax BJ to the starting solution enables the formation of a slightly less impact sensitive HMX/Licowax composite. It is assumed that the increase of the thermal effusivity through the addition of thermal conducting materials has a beneficial effect onto the explosives impact sensitivity.

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