SUBMICRON ENERGETIC MATERIALS BY COMMUNITION AND SUPERCRITICAL FLUID TECHNOLOGY

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Abstract

The formation of submicron particles of energetic materials (RDX and HMX) was under experimental investigation by two different techniques (comminution with an annular gap ball mill and supercritical fluid antisolvent crystallization). With both processes it was possible to produce material in the submicron range with a large specific surface area. The particles processed within the ball mill are distinguished by a very small particle size (mean value approximately 600 – 700 nm) and a nearly spherical shape. The PCA process leads to particles of about 1 µm with some larger particles in the sample. They obviously seem to be crystalline with a regular shape and a very smooth surface. The occurrence of agglomerates is typical for both processes. In the next step the sensitivity of the samples will be tested and compared with the sensitivity of microscale samples.

1. Introduction

Many product properties that are of relevance in the industrial use can be adjusted by changing the particle size and particle size distribution of the powder. This statement is valid in several fields ranging from polymers to pharmaceutical and inorganic powders.

In the case of solid explosives and propellants small particles are as a rule required to improve the combustion process. Indeed, the maximum energy output from a detonation of a solid explosive (ideal detonation) strongly depends on the particle size of the material.

Nanoscale particles of energetic materials with their large specific surface area can increase the loading of the energetic material in e.g. the PBX or solid rocket propellants. Combined with larger particles they can fill the voids between the micro-scale particles. The strong increase of the viscosity of the system limits the amount of nano-scale particles.

In this contribution two different micronization techniques will be presented and compared with each other. One is the suspension comminution in an annular gap ball mill, the other one is the use of a supercritical fluid as antisolvent. Both techniques are well known to

produce particles in the submicron range. The applicability of these processes to energetic materials (nitramines, RDX and HMX) will be presented in this paper.

2. Micronization by Comminution

3.1. Annular Gap Milling

Agitator ball mills comprise one of the largest groups of solids grinding apparatuses. Size reduction is accomplished in these mills when the bulk solid impacts freely flowing agitation balls within the grinding chamber. Agitator ball mills are used solely during wet grinding, i.e., a suspension of particles is ground by agitating balls within the grinding chamber. Such mills are used to grind colloids in the paint and coatings industry as well as for pharmaceuticals and other chemicals. The feedstock size is smaller than 100 µm and the final product is less than 5 µm [1].

The grinding chamber usually consists of a cylindrical container, but in the special case of the shear gap ball mill the grinding chamber is a flat gap between two rotating bodies. The agitating medium is usually spherical. Loads are imparted on the bulk solid when they are impacted by the balls or between the balls and the chamber wall. Types of loads include impact, compression and shear. Energy to set the balls in motion is imparted by stirring within the gap between the rotor and stator. The grinding chamber must be cooled during the operation, because the majority of the energy imparted is transformed into heat.

For our experiments we used an annular gap mill from Hosokawa Alpine RSK 50 with a milling volume of 150 ml.

The advantage of annular gap ball mill compared with conventional agitator ball mills is the very narrow energy spectrum required for the operation and the correspondingly small residence time distribution of the material. As a result, very narrow particle size distributions can be obtained. In addition, the grinding chamber volume to the radiating surface ration is very favourable, so that this method is very well suited for thermo labile substances.

Annular gap mills can easily be up-scaled so that the capacity can easily be increased to production scale.

Figure 1 shows a processing scheme of the facility. The rotor as well as the stator of the mill is coated with polyurethane. The frequency of the mill was 8000 rpm. The material passed 20 times the comminution zone. Milling balls consisted of zirconium oxide.
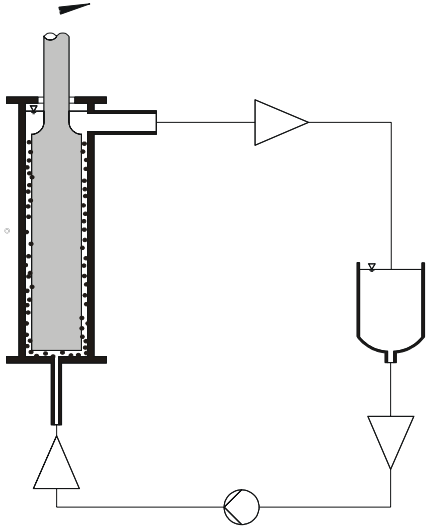
Figure 1: Processing scheme of the milling facility

3.2. Materials and Method

For a screening of the applicability of the mill for size reduction of energetic materials we comminuted two different explosives, Hexogen (RDX) and Octogen (HMX). All explosives were comminuted in water because of their insolubility in it. The suspension concentration was 10 wt.-%. The material passed 20 times the comminution zone. Afterwards the materials were characterized by particle size and size distribution coefficient. The distribution coefficient ξ of their particle size distribution is determined by:

$$\xi = \frac{x_{84,3} - x_{16,3}}{2 \cdot x_{50,3}} \tag{1}$$

where $x_{i,3}$ denotes particle size at particle size distribution i%. It was measured by laser diffraction spectrometry. It is an optical technique that evaluates the scattered light to determine the distribution. Also the optical appearance was investigated by SEM (scanning electronic microscopy), the specific surface area was determined by BET method and the particle density was measured by gas pycnometry.

3.3. Results

Figures 2 and 3 show the particle size distribution of the original material and the comminuted product. As you can see, we could perform very effective grinding down to submicron range. The results from laser diffraction spectrometry should only be considered indicatory. In the evaluation process of the measurement is the knowledge of the exact

diffraction index essentially for small particle sizes. RDX and especially HMX have very different diffraction indices depending on the considered crystal surface.
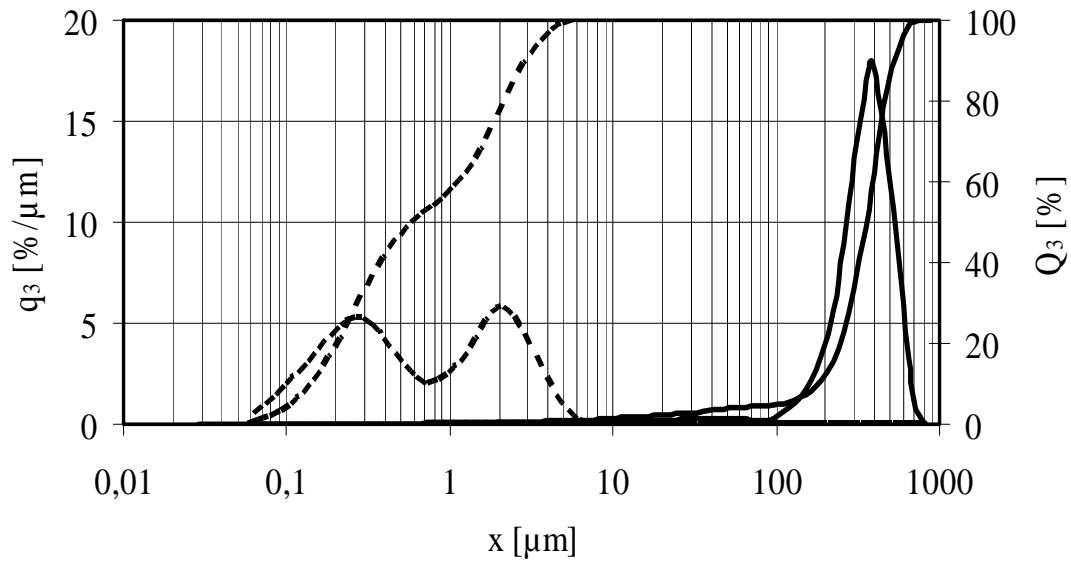

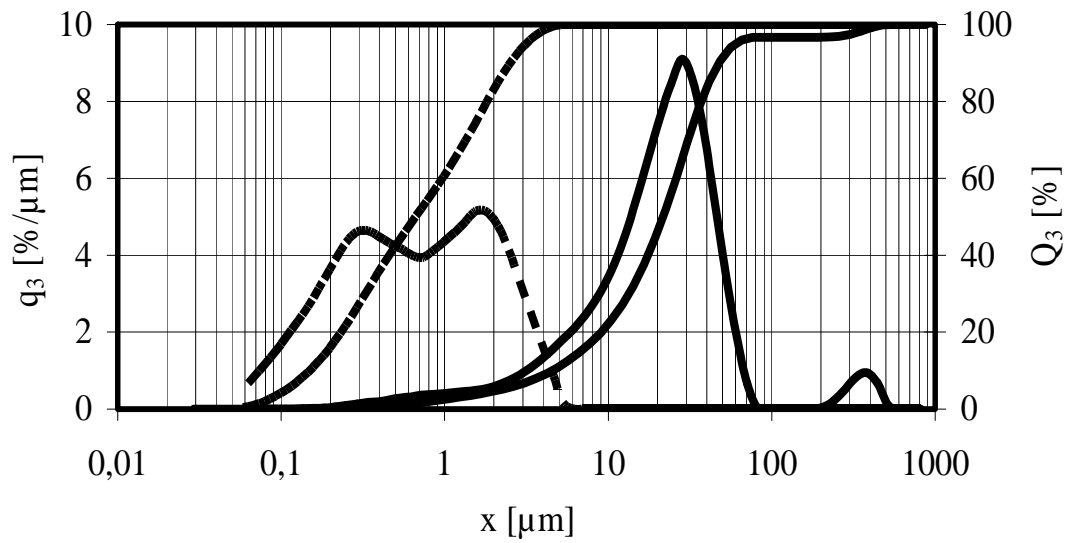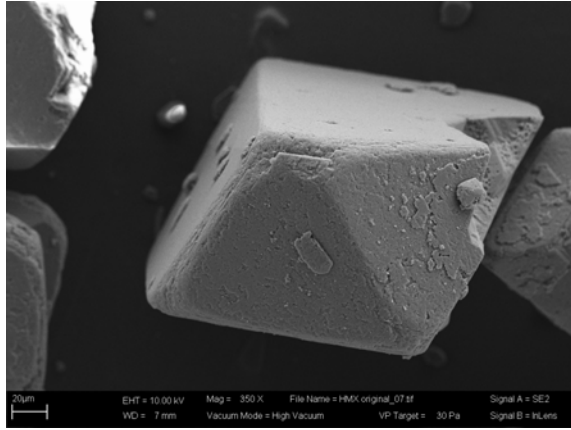*Figure 2: Original HMX (continuous line) and comminuted HMX (dotted line)*
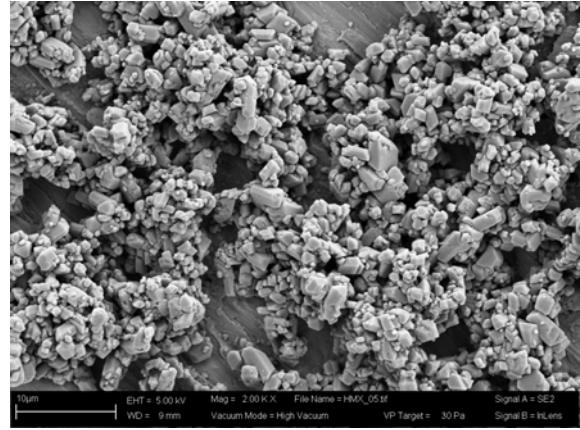

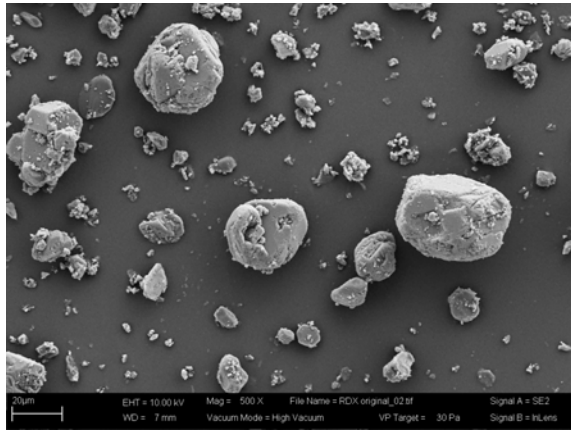*Figure 3: Original RDX (continuous line) and comminuted RDX (dotted line)*

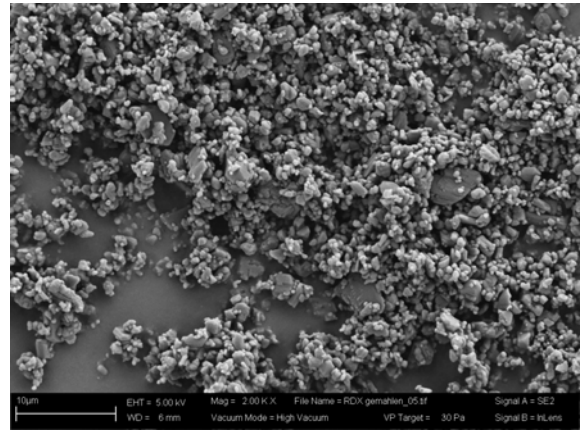Figure 4 shows the SEM pictures of the original and processed material.

HMX original material

HMX comminuted

RDX original material

RDX comminuted

Figure 3: SEM images of original and comminuted nitramines

As you can see from the particle size analysis and the SEM pictures we generated very fine material with a mean diameter of approx. 1 µm. This material has a very spherical shape and smooth surface.

All characterization data of the raw and processed materials are summarized in Table 1. We also performed impact and friction sensitivity tests with the materials. We didn't observe any significant change in these parameters due to the grinding process. We will continue the characterisation by GAP tests to pinpoint the sensibility in the PBX matrix.

Table 1: Summary of the characterization of the raw and processed materials

| Substance	Sample	$x_{50,3}$ [µm]	S_{BET} [m^2/g]	ρ [g/cm^3]	Impact [Nm]	Friction [N]
RDX	raw	21.7	0.61	1.902	5.0	120
	milled	0.66	3.83	1.942	4.0	96
HMX	raw	355	0.26	1.923	7.5	108
	milled	0.58	4.11	1.951	7.5	96

3. Micronization by Supercritical Fluid Techniques

Supercritical fluids are compressed gases that are used at temperatures and pressures higher than their critical point. They, in principle, do not give problems of solvent contamination since when the decompression occurs they are completely released from the solute. The most common supercritical fluid is CO_2 since it has relatively low critical parameters ($\vartheta_c = 31.1\ °C$ and $p_c = 7.38\ MPa$), it is not toxic, non flammable and cheap. The operating conditions for supercritical fluids processing are generally mild, thus giving no problem to process "heat sensitive" materials. Also, the control of particle size and particle size distribution of the micronized material promises to be relatively simple to be obtained by continuously varying the process conditions.

Precipitation with a Compressed Fluid Antisolvent (PCA) is the most promising supercritical technique since it has been demonstrated that it is capable to produce controlled micronic and sub-micronic particles [2, 3]. In the PCA process the supercritical fluid substitutes the liquid antisolvent and causes the precipitation of solute since it forms a solution with the primary solvent. Therefore, a pre-requisite to perform PCA is that the process is performed at temperature and pressure conditions at which complete miscibility exists between the primary liquid solvent and the supercritical antisolvent. A distinctive characteristic of supercritical fluids is the diffusivity that can be up to two orders of magnitude higher than those of liquids. Therefore, the diffusion of the supercritical fluid into a liquid solvent can produce a fast supersaturation of solute dissolved in the liquid and its precipitation in micronized particles.

3.1. Apparatus and Method

The experimental work was performed in a high pressure pilot plant, consisting of the CO_2 supply unit including membrane pump and heat exchanger, the precipitation vessel (volume: 500 ml) with sinter metal filter and the membrane pump connected with the nozzle placed at the top of the precipitation vessel (see Fig. 4, schematically). The mass flow rate of the CO_2 is limited to 30 kg/h, the maximum volume flow of the solution is 600 ml/h.

Figure 4: Schematic view of the high pressure pilot plant (PCA process)
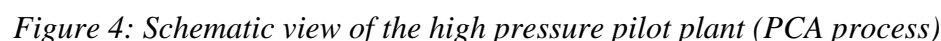
At the beginning of the continuous PCA process, CO_2 is fed to the precipitation vessel until the desired pressure is reached. Then a steady antisolvent flow is set, the flow rate of which is controlled at a designated value. After the steady state is maintained for 10 minutes the solution is sprayed into the precipitation vessel through a nozzle. The particle formation can be observed through sapphire windows which are placed on different positions in the separation vessel. Nucleation occurs as a cloud formation after leaving the nozzle exit, where the droplets of the solution expand and dissolve into the CO_2 phase. Simultaneously, the antisolvent diffused into the droplets which leads to a swelling of the droplets and precipitation occurs in the droplets. The particles produced are collected on a sinter metal filter (pore size: 100 nm) placed on the bottom of the precipitation vessel. In order to remove any residual organic solvent from the particles pure CO_2 continues to flow for at least 10 minutes through the precipitation vessel before starting the depressurization of the precipitator. If this purging step with pure CO_2 is not done, organic solvent condenses during the depressurization and partly dissolves the powder modifying its morphology and lowering the yield. The fluid mixture (mainly CO_2 and some organic solvent) leaves the precipitation vessel and is depressurized in the separator where solvent is separated from the CO_2. The CO_2 can be recompressed and fed into the CO_2 cycle or let off. Samples of powders precipitated are characterized by scanning electronic microscopy (SEM), laser light diffraction (particle size distribution, Mastersizer S, Malvern), particle density (gas pycnometry, Ultrapycnometer,

Quantachrome) and BET absorption measurement (specific surface area, Nova 2200, Quantachrome).

3.2. Results

In order to compare the micronization by the PCA process with the comminution in the annular gap ball mill, hexogen (RDX, cyclotrimethylene trinitramine) and octogen (HMX, cyclotetramethylene tetranitramine) were processed. The precipitation of both materials were carried out from γ-butyrolactone (solute concentration: 10 wt.-%). The precipitation pressure and temperature were 15 MPa and 40 °C, respectively. A 20 kg/h mass flow rate of CO_2 and a 300 ml/h flow rate of solution were adjusted.

In Table 2 the results of these experiments are summarized. Figures 5 and 6 show the particle size distributions of the raw and processed samples.

Table 2: Summary of the characterization of the raw and processed materials

Substance	Sample	$x_{50,3}$ [µm]	S_{BET} [m^2/g]	ρ [g/cm^3]	Impact [Nm]	Friction [N]
RDX	raw	21.7	0.61	1.902	5.0	120
	PCA	10.8	1.90	1.811	7.5	96
HMX	raw	355	0.26	1.923	7.5	108
	PCA	7.6	1.67	1.939	6.0	120

It becomes clear that the size of the particles is larger than the mean size of the milled particles. The impact and friction sensitivity is in the same region of the values of the unprocessed samples. In comparison to the comminuted RDX the precipitated RDX seems to be less sensitive.
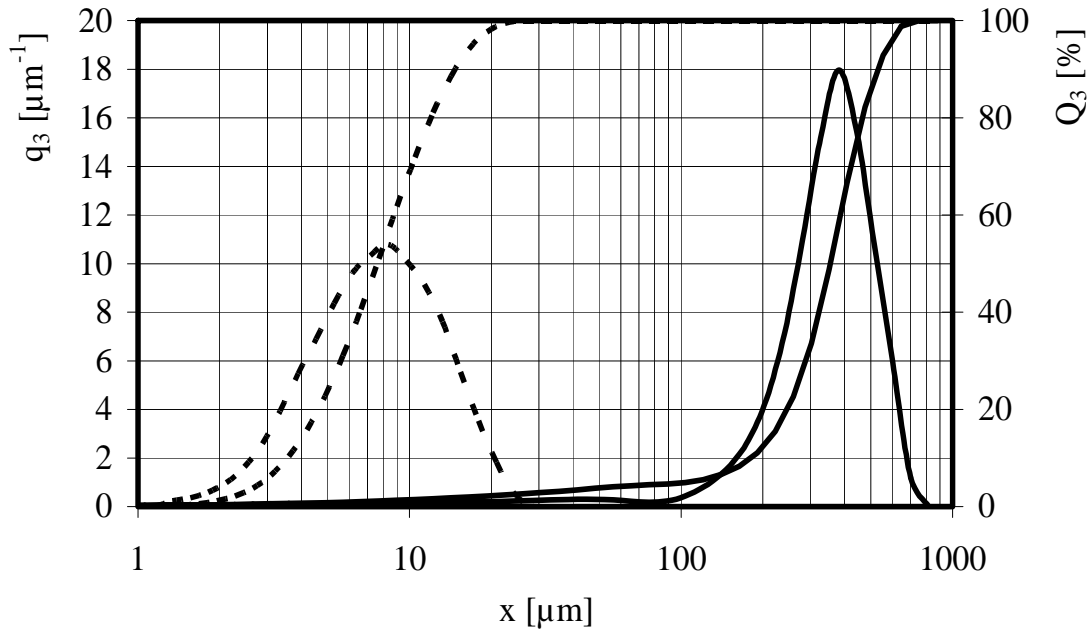
Figure 5: Original HMX (continuous line) and micronized HMX (dotted line)
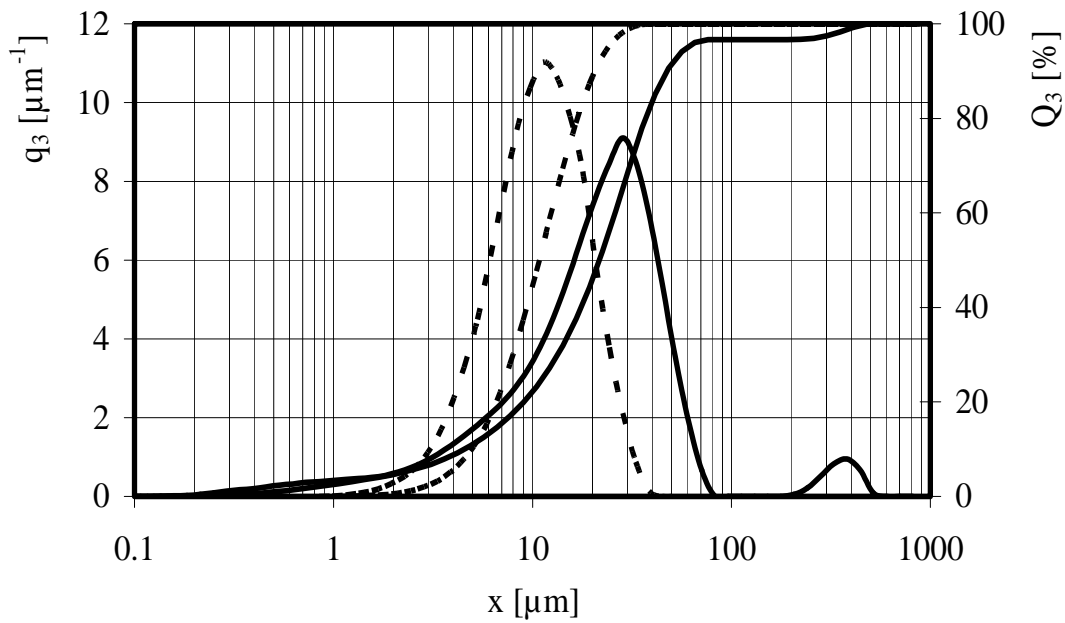

Figure 6: Original RDX (continuous line) and micronized RDX (dotted line)

An optical perception of the shape, morphology and size of the micronized material is given in the following SEM pictures (Fig. 7 and 8).
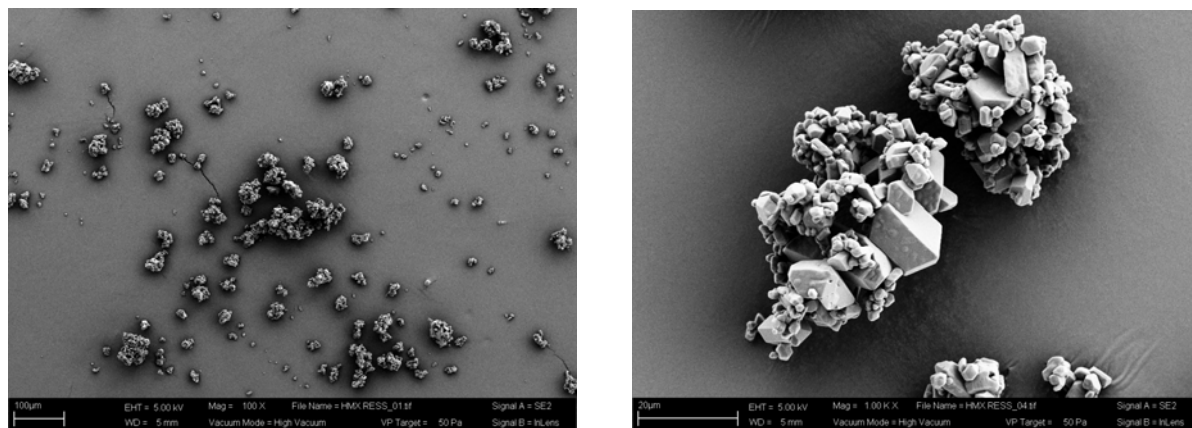
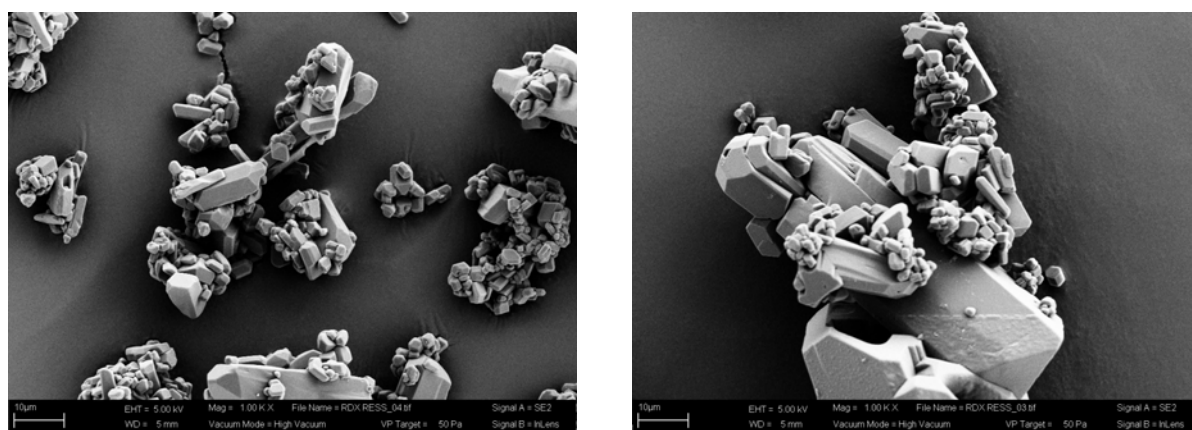*Figure 7: SEM pictures of processed HMX particles (PCA process)*

Figure 8: SEM pictures of processed RDX particles (PCA process)

The material seems to be crystalline and the particle surface is very smooth. Strong agglomerates are present but also the particle size distribution of the primary particles is relative broad. Especially some few large particles can be observed onto their surface small particles stick.

4. Conclusions

It was possible to micronize nitramines by comminution with an annular gap ball mill as well as by supercritical fluid technology (PCA process). The comminuted nitramines are distinguished by a very small mean particle size (600 – 700 nm) and a spherical morphology. The precipitated samples have a mean particle size in the range of about 10 µm. The crystal shape is marked so that a high crystallinity of the material can be assumed.

To complete the characterization of the samples X-ray diffraction measurements and gap tests will be carried out. By means of these measurements an assessment of sensitivity of the micronized particles by different processes will be possible.

5. Literature

[1]   U. Teipel, I. Mikonsaari, "Size reduction", in: Energetic Materials, Particle Processing and Characterization, U. Teipel (Ed.), Wiley-VCH, Weinheim, 2004

[2]   E. Reverchon, "Supercritical antisolvent precipitation of micro and nano particles", *J. Supercrit. Fluids* 15, 1-21 (1999)

[3]   J. Jung, M. Perrut, "Particle design using supercritical fluids: Literature and patent survey", *J. Supercrit. Fluids* 20, 179-219 (2001)