Production and Characterization of Nanocrystalline Explosive RDX

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Introduction

High explosives including the nitramines RDX, HMX, and CL-20 are dangerously susceptible to unintended initiation by stimuli such as shock and impact. The sensitivity of these materials tends to increase with the energy density. TNT, for example, is relatively insensitive, however, its power is significantly lower than RDX. On the other hand CL-20 and HMX are significantly more sensitive than RDX but also more powerful. RDX is often preferred in munitions due to its balance of power and sensitivity. However, further desensitization of RDX is desired.

Initiation of a secondary explosive as a result of an external stimulus is believed to result from non-homogeneous distribution of the incident energy(1,2). Energy from a shock wave or an impacting object is believed to localize and generate hot spots within the explosive. Hot spots of sufficient size and temperature can initiate the surrounding explosive material and lead to a detonation of the entire charge. The localization of energy is likely due to voids present within the explosive(1). These can be found in the interstitial space as well as within the individual crystals. Compression of such voids leads to hot spot formation. The size of the void prior to compression is significant as it influences the final temperature of the hot spot. Voids below a certain critical size may not heat to a sufficient temperature to initiate a larger explosion. In addition, small hot spots may not contain enough energy for a sustained reaction in the surrounding medium. Rather, the energy can dissipate by conduction without an explosion.

This effort is aimed at minimizing the inter- and intra-crystalline void size by reducing the crystal size down to the nano-scale. As a result no large voids can be present within the crystals and voids between crystals are limited to a very small size. By reducing the crystal size a matrix is created where the number of inter-crystalline voids is greatly increased, but the size of these voids is greatly decreased. In such arrangement it is conceivable that incident energy from a shock wave or an impact may be distributed more homogeneously, resulting in a reduced chance of initiation.

Background

Previously we demonstrated that nano crystals of RDX could be produced by recrystallization *via* rapid expansion of supercritical solutions (RESS) with carbon dioxide as the solvent(3,4). A saturated solution of RDX in supercritical carbon dioxide was prepared at

the desired pressure and temperature. The solution was than expanded through a nozzle to atmospheric pressure. As a result of rapid expansion the RDX precipitated forming fine, nearly uniform particles.

The RDX particles were shown to be crystalline by Powder X-Ray Diffraction. A high purity product was achieved as a result of having no organic solvents present. The crystal exhibited round or oval shape with no apparent surface features. The nanocrystalline RDX was found to have a melting point nearly identical to the melting point of RDX with conventional grain size.

The RESS process was characterized. The effect of the pre-expansion pressure and temperature on the final particle size was investigated. It was found that increasing the saturator temperature and pressure lead to a decrease in the particle size. Crystals with a mean size as small as 100 nm with a narrow size distribution were obtained.

Experimental

For scaling the RESS process by an order of magnitude or higher, recycling of carbon dioxide becomes increasingly important. As a result of low solubility of RDX in supercritical carbon dioxide(5) (ca. 1g RDX/ 5 kg CO_2) large quantities of CO_2 must be processed. Recycling of CO_2 entails liquefaction of the gas in order to be fed back to the pump. This may be achieved in two ways, cooling the expanded gas until liquid is formed or by compression of the gas followed by cooling.

An experimental set-up, depicted in Figure 1, was built having the capability to recycle carbon dioxide by cooling and compression. The set-up consists of a piston pump for pumping liquid carbon dioxide to the saturation vessel. The pressurized carbon dioxide is pre-heated before the saturator. The saturated solution is expanded through a nozzle into a collection vessel. Depending on the expansion pressure the carbon dioxide is recycled either by cooling or by compression using a two-stage diaphragm compressor.

When operating the RESS process with the expansion pressure around 1 bar, condensation by cooling alone become impossible, since the triple point of carbon dioxide is located near 5 bar and -56 ^{o}C. Therefore, a compressor is required to compress the carbon dioxide to around 40 bar or higher. At such pressure liquefaction can be achieved at above 0 ^{o}C, which is readily attainable with conventional chillers.

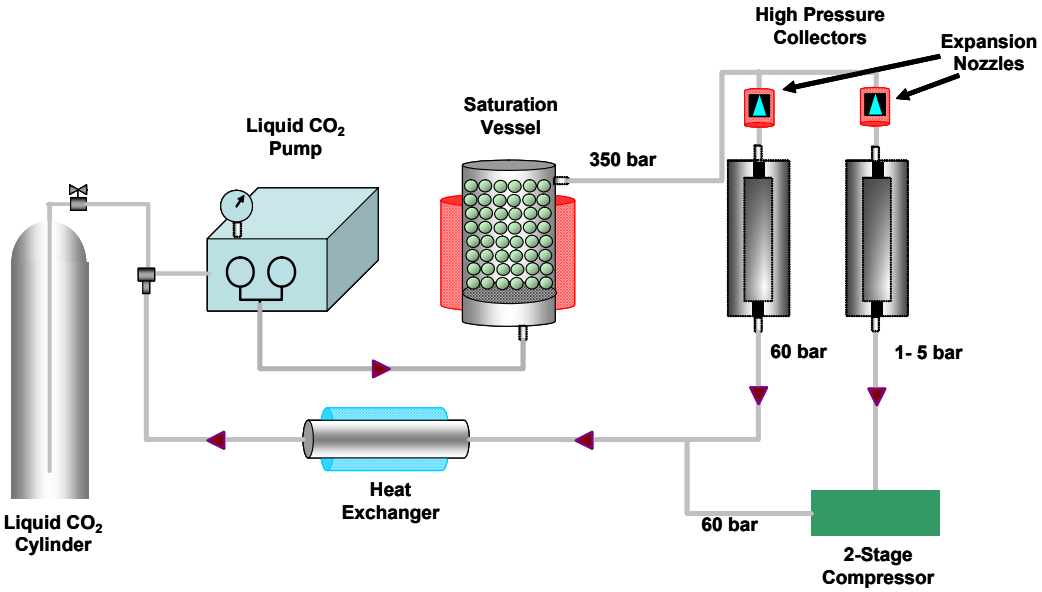

Figure 1. Experimental set-up.

An alternative process regime was attempted to eliminate compression. Instead of expansion to atmospheric pressure, the expansion pressure was set at 60 bar. The effect of increasing the expansion pressure on the particle size was investigated. The effect of increasing the discharge pressure up to 60 bar is illustrated for two pre-expansion conditions, 85 ^{o}C and 280 bar and 85 ^{o}C and 350 bar (Figure 2).

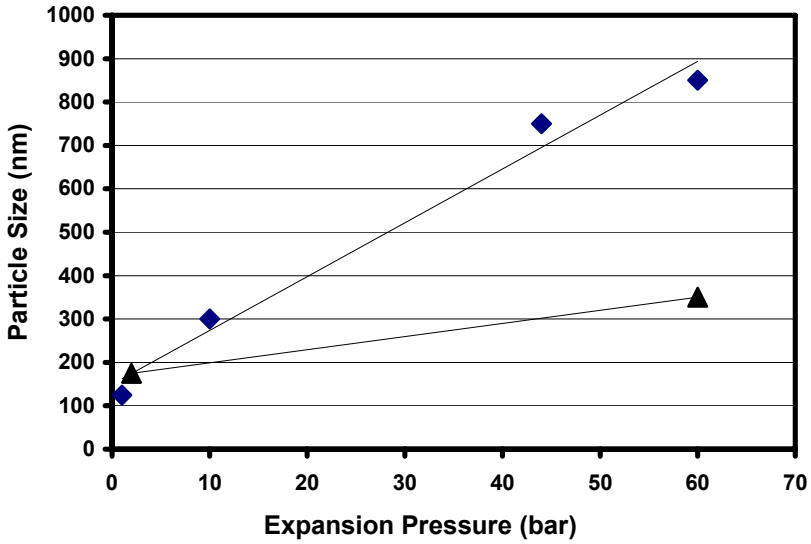

Figure 2. The effect of expansion pressure on the particle size at pre-expansion pressures of 280 bar (diamonds), 350 bar (triangles).

As can be seen in Figure 2, the particle size increases with expansion pressure. However, it is possible to reduce the particle size by increasing the saturator pressure. The particle size was reduced by more than a factor of 2 when the pre-expansion pressure was increased from 280 bar to 350 bar. The mean particle size obtained with the pre-expansion pressure set at 280 bar

was around 850 nm and with pre-expansion pressure set at 350 bar the mean particle size was around 350 nm. At low expansion pressure the finest particles are obtained. By expansion from 350 bar to 3.5 bar the mean particle size of RDX was around 150 nm. An SEM image of the particles produced is shown in Figure 3.

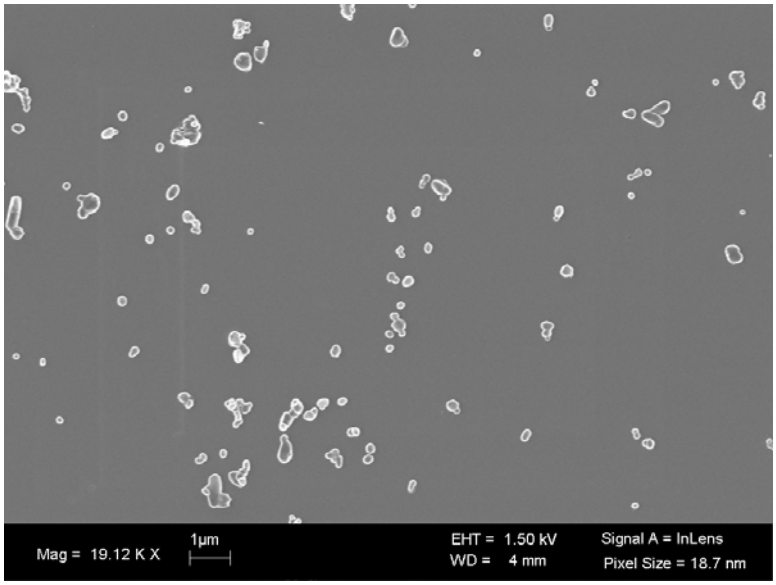

Figure 3. SEM image of RDX recrystallized by expansion from 350 to 3.5 bar.

RDX obtained by expansion from 350 bar to 60 bar had a mean particle size around 350 nm. An SEM image of is shown in Figure 4.

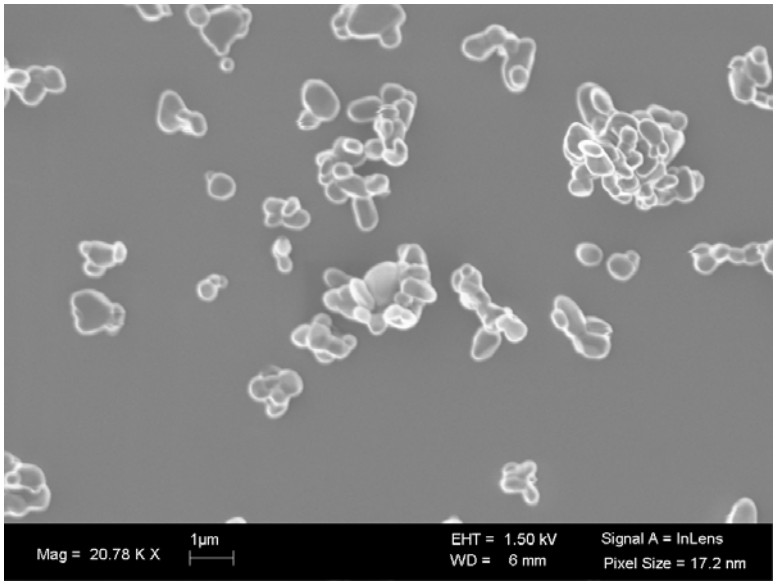

Figure 4. SEM image of RDX recrystallized by expansion from 350 to 60 bar.

Initiation Sensitivity

Samples of pure nanocrystalline RDX as well as compositions containing nanocrystalline RDX were tested for initiation sensitivity. Sensitivity to shock and impact were tested. Compositions were prepared with 88 % RDX and 12 % wax binder. The compositions were prepared by slurry coating. Holston produced 4.8 micron RDX and class 5 RDX were used as the reference materials.

The impact sensitivity tests were performed using an ERL, Type 12 impact tester, with a 2.5 kg drop weight(6). The sensitivity is represented by the drop height at which initiation probability is 50% (H_{50}). Shock sensitivity analysis was performed by the NOL Small Scale Gap Test method(7). Samples were pressed into brass cylinders at 16,000 psi. The sensitivity to shock is presented as the shock pressure necessary for 50% initiation probability of the sample.

The impact sensitivity was measured for samples in loose powder and in pellet forms. The sensitivity for the loose 150 nm RDX was over 100 cm, for 150 nm RDX pressed into pellets the H_{50} was 42 cm. The H_{50} for 350 nm RDX in the loose form was 73.5 cm, and for dense pellets was 35.5 cm. The H_{50} for loose 4.8 micron RDX was 32.2 cm. The H_{50} for class 5 RDX was 24 cm. For compositions containing 150 nm and 350 nm RDX the H_{50} values were 46 cm and 62 cm respectively. For the composition containing 4.8 micron RDX the H_{50} value was 26 cm.

Shock sensitivity results were obtained for samples of RDX with a mean size 150 nm, 350 nm, and 4.8 micron. The composition was prepared by slurry coating. As the shock sensitivity of an explosive formulation depends on the density of the pressed sample, the densities are also included. Figure 5 shows the effect of the density of pressed RDX on the shock initiation sensitivity. The data shown are that for conventional RDX. As can be seen, the shock sensitivity is greatly reduced as the density approaches the theoretical maximum (1.82 g/cc).

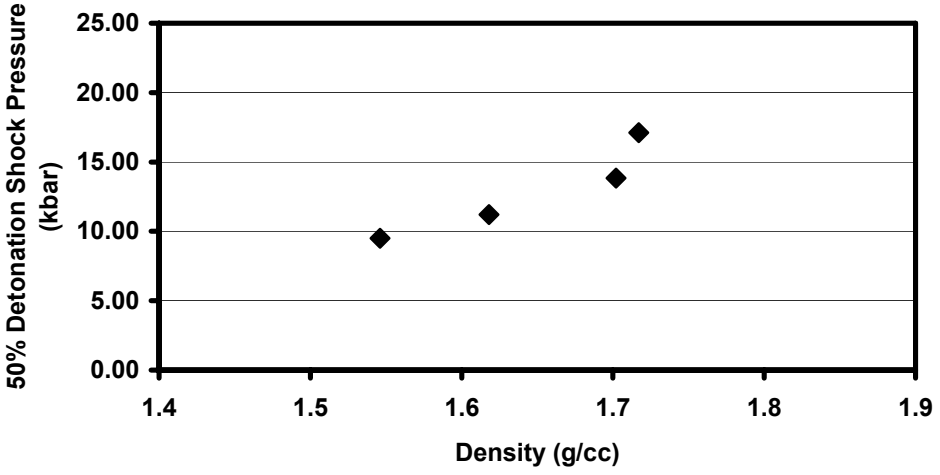

Figure 5. Effect of density on shock sensitivity of conventional RDX

The densities for the three tested samples were found to be around 1.57 g/cc. The shock sensitivity of the sample containing the 150 nm RDX was 25 kbar, 350 nm RDX was 32 kbar, and the 4.8 micron RDX was 21 kbar. A sample of uncoated 150 nm RDX was also pressed at 16,000 psi. The density attained with 16,000 psi pressing was 1.42 g/cc. The shock sensitivity for this sample was measured at 20.6 kbar. A lower pressing density of 150 nm RDX compared with conventional RDX is an indication of an increased mechanical strength of the powder. This is consistent with reports of increased mechanical strength as a result of nanoscale grain size. Pressing at higher pressure would be required to attain a higher density. The shock sensitivity for this sample is significantly lower than for conventional RDX at such pressing density (see Fig. 4). This may be an indication that even at low density the average inter-crystalline void size is much smaller than for larger RDX crystals. Consequently, having a larger number of smaller voids leads to a reduced initiation sensitivity vs. a smaller number of larger voids.

Summary

Production of nanocrystalline RDX at elevated expansion pressures was investigated. Increasing the expansion pressure from 1 bar up to 60 bar results in an increased particle size. At high expansion pressure, the particle size is strongly dependent on the pre-expansion pressure within the saturator. Increasing the pre-expansion pressure from 280 to 350 bar, the mean particle size is reduced by over a factor of 2. Operation of the RESS process with high expansion pressure is significantly less energy consuming. However to attain particle size below 200 nm it may be essential to expand to lower pressures.

The response of recrystallized RDX to initiation stimuli such as impact and shock was compared to the response of conventional RDX. The preliminary finding indicate that samples consisting of pure nanocrystalline RDX as well as compositions with 88% RDX and 12 % binder show a significant reduction in sensitivity with respect to conventional RDX.

References

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