Analysis of Safety and Characterization on Nano RDX Produced by Wet Grinding

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Abstract. Under water environment, nanometer RDX was produced by wet grinding. With the help of Zetasizer Nano, field emission scanning electron microscope, Custer type hammer instrument, its particle size distribution, morphology appearance, the sense and other properties were characterized and then the safety of the process of crushing was analyzed. The experimental results show that the sensitivity of nanoscale RDX prepared by wet method is significantly reduced and the safety is improved. Due to the low cost of this method, it is possible to reuse large-scale recycled RDX, which solves the difficulties of storing and transporting the RDX and expands its scope of use.

1. Introduction

A type of rocket, which was installed in the late 1980s, has now entered a waste period. Its warhead is equipped with TNT-RDX-Al, and traditional non-military technology treatment is open burning or detonation, which not only pollutes the environment, but also causes waste of resources. At present, the technology has been able to separate and recover three energy components of TNT, Al and RDX [1-4]. TNT and Al can be used directly for industrial reuse, while RDX is still an outstanding issue because of its high sensitivity and high risk factor.

RDX is a widely used high-energy explosive and has a high industrial value. However, the RDX recovered has a large sensitivity and is so dangerous. It is neither convenient for transportation nor for storage, which greatly limits its use. The top priority is to reduce RDX sensitivity so that it can be applied to industry. Many researchers are committed to reducing RDX sensitivity and have achieved fruitful results. The fact shows that the particle size of RDX has a significant impact on performance. Chen et al. [5] dissolved common RDX in a mixed solvent and prepared nano-RDX powders by spray drying. The impact sensitivity characteristics are about twice as high as that of micro-meter RDX. Song et al. [6] adopted sol-gelation, which adopts the method of first introducing and then re-etching Fe ions to finally obtain RDX nanoparticles. The mechanical sensitivity test shows that the impact sensitivity of nano-RDX is slightly lower than that of micro-meter RDX. Norbert Radacsi et al. [7] prepared high-quality sub-micron using electrospray method. Grade RDX crystal, its impact sensitivity from 7.5J to 10.0J, friction sensitivity increased from 120N to 360N or more. Victor Stepanov et al. [8] used supercritical fluid technology to obtain RDX crystals with a particle size range of 110-220nm. They tested the sensitivity of RDX coated and uncoated paraffin, and the results showed that RDX did not ignite at the maximum energy load of 0.25J.

These studies, because of the harsh conditions and high costs, can only be tested in the laboratory, and do not have the capability of large-scale production. There is a need for cheaper and more practical methods to produce nanometer-scale RDX with lower sensitivity. The author started with the theory of heat conduction and analyzed the safety of mechanically crushed RDX, and chose cheap water as the heat transfer medium. Finally, under the water environment, the improved ball mill
machinery crushed the RDX recovered from the discarded TNT-RDX-Al explosives, successfully prepared nano-RDX, which provided a new idea for the reuse of waste explosive resources.

2. Safety analysis
RDX is a sensitive type of high-energy explosive. While mechanically crushed, the safety is the most important. In this experiment, water was chosen as a coolant to disperse the heat generated by the mechanical work and fragmentation of the explosive in a timely manner to avoid heat accumulation, and thus the temperature of explosive explosion could not be established in the system. Too little water is not enough to take away the heat generated by the system during the crushing process, which can easily lead to an explosion accident. Excessive water volume can add to the dehydration work. Therefore, through the conservation of energy and the law of heat transfer, it can be calculated that there must be an optimal value of the amount of water used in the comminution process to both ensure safety and reduce the difficulty of dewatering.

- \( Q_j \) is the mechanical energy required to crush explosive: \( Q_j = q_j m_E \)  
- \( Q_s \) is the energy released by RDX in the event of an explosion: \( Q_s = q_s m_E \)  
- \( Q_{wq} \) is the heat carried away by water and water vapor: \( Q_{wq} = C_w m_{wq} (T_r - T_o) + C_q m_q (T_r - T_l) \)  
- \( Q_{wq} \) is the absorbed heat water converted from liquid to gaseous: \( Q_{wq} = q_{wq} m_{eq} \)  
- \( Q_e \) is the energy that the RDX must give when it explodes: \( Q_e = C_E m_E (T_E - T_l) \)

Assuming that the comminution system is closed, there is no energy exchange with the outside world. According to the law of conservation of energy, no explosion must meet the following formula: 
\[ Q_j + Q_s \leq Q_{wq} + Q_{wq} + Q_e. \]

This derives the formula for calculating the amount of water:
\[ m_{wq} \geq \frac{q_j + q_s - C_E (T_E - T_o)}{C_w (T_r - T_o) + C_q (T_r - T_l) + q_{wq}} \]  

In the formula, \( q_j \): the energy needed to crush the unit mass explosive (kJ/kg); \( m_E \): the mass of the explosive (kg); \( q_s \): the explosion heat of the ladder black aluminum explosive (kJ/kg); \( m_{wq} \): the mass of water (kg); \( C_w \): specific heat capacity of water (kJ/kg·℃); \( C_q \): specific heat capacity of water vapor (kJ/kg·℃); \( T_o \): initial temperature of water (℃); \( T_l \): critical temperature when water changes from liquid to vapor (℃); \( T_E \): flash point during the 5s lag phase (℃); \( q_{wq} \): vaporization heat of the water (kJ/kg); \( C_E \): specific heat capacity of the TNT-RDX-Al explosive (kJ/kg·℃). Looking at the empirical data of each parameter in equation (6) [9,10], the ratio of water/RDX can be calculated as 1.87, which means that the theoretically added water quality is 0.87 times more than that of explosives to ensure crushing safety.

3. The Experiment

3.1. Materials and Instruments
Materials: RDX, according to the literature [4] experimental method, acetone as solvent, purity 98.4%, impact sensitivity 76%. Surface active agent, high alcohol ester natural surfactant and polyoxyethylene polyl nonionic surfactant mixture, self-prepared.

Instrument: circulating water multi-purpose vacuum pump, SHB-3 type, Zhengzhou Duyu Instrument Factory; electric centrifuge, 800 type, Jintan Fuhua Instrument Co., Ltd.; vacuum drying box, ZK35 type, Tianjin North China Experimental Instrument Co., Ltd.; Electron microscope, JSM-5800, Japan Co., Ltd.; Nano laser particle size analyzer, HAS-3000 type; improved ball mill, 4kW, three-speed control.

3.2. Preparation of Nano-RDX
RDX has a higher sensitivity, and direct mechanical smashing can easily lead to igniting accidents. To ensure safety, wet grinding is used and water is selected as a coolant. The RDX is mixed in water and
stirred, mixed with a composite surfactant, prepared into a slurry, and uniformly added into a laboratory ball mill to control the rotation speed and the number of grinding times. After the electric centrifuge is continuously dehydrated, it is completely dried in a vacuum drying oven.

3.3. Sensitivity Test
The impact sensitivity was measured according to the GJB772A-97 method 601.1\textsuperscript{11}. We limited the specimen between two smooth hard surfaces, and dropped the hammer to fall freely, observed and calculated the explosion probability, and characterized the impact sensitivity of the specimen.

Test equipment: Castel falling hammer.

Test conditions: dose (50 ± 1) mg, drop weight (10.000 ± 0.010) kg, drop height (25.0 ± 0.1) cm, temperature 10–35 °C, relative humidity ≤80%. When it was observed that there were explosions, luminescence, smoke, discoloration of the sample, traces of the surface of the striker that came into contact with the sample, and odor of decomposition or explosive gas products, they were all judged to an explosion, otherwise they were judged to be unexploded.

4. Results and Discussion

4.1. Particle Size Distribution and Morphology Characterization
The amount of water added to the RDX slurry should be appropriate. The ratio of control water to RDX in this experiment is 2.0. The composite surfactant dissolved in water has good alcohol solubility. After grinding, it was washed with ethanol. After several times of washing, the composite surfactant coated on the surface of RDX crystals could be washed away. Then placed in a vacuum oven, controlled the temperature at 10 °C, 20 °C, 30 °C. Drying for 2 hours, there were crystals precipitated. The experimental phenomenon is shown in Figure 1.

![Figure 1. Crystallized RDX after smashing](image)

The particle size and distribution were measured with a laser particle size analyzer (Figure 2). As can be seen from Figure 2, the pulverized RDX is of nanometer size, and the particle size ranges from 60 nm to 130 nm, and the distribution is uniform. According to the analysis, the raw material RDX is subjected to uniform force fields such as extrusion, impact, and shear in the ball mill, gradually forming regular small particles. The composite surfactant is coated on the particle surface during the RDX grinding process, which limits the growth of RDX crystal and also prevents the reintegration of RDX powder. The small particles, under the repeated action of the uniform force field, become nanoparticles.
Figure 2. Distribution curves of nanometer RDX

The surface of the RDX product was scanned using a field emission scanning electron microscope focused electron beam, as shown in Figure 3. It can be seen that after mechanical crushing, RDX dispersion is relatively uniform, there is no obvious agglomeration phenomenon, the crystal shape is relatively regular, the defects are few, similar to the potato shape, and the edges and corners are not obvious.

Figure 3. SEM photos of recrystallized RDX

4.2. Sensitivity analysis

A comparison of the explosion and the absence of an explosive impact is shown in Figure 4. It can be seen that there are obvious explosion marks on the surface of the hitting explosion. At the same time, experimental phenomena such as light emission and smoke emission can also be observed during the experiment. On the contrary, in the absence of an explosion, only the explosive on the surface of the pillar is compacted. Through observation and analysis, it can be judged whether explosives exploded during the impact, and then the impact sensitivity of RDX explosives was calculated.

Figure 4. The columns after experiment
Test results: the probability point of the explosion was 49%, and the confidence interval of 0.95 was (0.29, 0.70). Compared to the raw material RDX (76%), the sensitivity value decreased by 27%. From the test results, the mechanical impact sensitivity decreases with the particle size of RDX decreasing. Interestingly, this is inconsistent with the conclusion that "the smaller the particle size is, the higher the impact sensitivity is," [12]. Why? Based on the analysis of explosives hotspot theory, the nano-RDX in this experiment has two ways to form hot spots under mechanical action: micro-bubbles contained in explosives are adiabatically compressed; localized heating of explosives due to friction (such as between explosive particles, explosives and impurities or friction with the inner wall of the container). From the results of 3.1, the nano RDX products in the experiment have smooth surfaces and regular shapes. Therefore, the adiabatic compression is not easily formed in the particles, and the mutual friction is small, and it is difficult to form hot spots. Further, the mechanical impact sensitivity is greatly reduced.

5. Conclusions
(1) The RDX recovered from waste ladder black-aluminum mixed explosives can be wet-milled in a water environment. To ensure operational safety, the mass ratio of water/RDX should exceed 0.87.
(2) After RDX is crushed to nanometer level, the shape is regular, the particle size is uniform, and the mechanical sensitivity is reduced significantly. It can be used as a high-energy insensitive explosive.
(3) The low cost of wet preparation makes it possible to reutilize large amounts of recycled RDX on a large scale, which can provide a reference for the recycling of waste black aluminum mixed-metal charges.

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