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Surface defects and their role in the shock sensitivity of cyclotrimethylene-trinitramine

Victor J. Bellitto [a,*], Mikhail I. Melnik [b]

[a] Naval Surface Warfare Center, Research & Development, Building 600, 4104 Evans Way, Suite 102, Indian Head, MD 20640-5102, United States
[b] Department of Commerce, PO BOX 2201, Niagara University, NY 14109-2201, United States

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ABSTRACT

The surface of cyclotrimethylene-trinitramine (RDX), a commonly used crystalline explosive was studied using atomic force microscopy (AFM). A diversity of surface defects was observed in different RDX particles as well as different parts of the same particle. Statistical analysis was undertaken to model the observed surface characteristics with the known shock sensitivities of the material. To quantify the surface defects observed on the crystalline surface of the RDX particles, surface roughness measurements were acquired. It was determined that there exists a statistically significant relationship between surface roughness characteristics and the shock sensitivity of the material.

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1. Introduction

A long sought after goal in energetic materials research has been the development of explosives and propellants with insensitive properties. The production of insensitive munitions has the potential to reduce the hazards of munitions storage and transport as well as the potential to increase storage and transport capabilities. Cyclotrimethylene-trinitramine (RDX), a crystalline explosive, is one of the most stable high explosives and a widely used energetic material in military applications. It has also been the focus of much research interested in obtaining a relationship between its crystalline properties and its shock sensitivity. The interest has been highlighted with the formation of the Reduced-Sensitivity RDX Round Robin program, an international inter-laboratory comparison investigation [1]. Early investigations have reported that particle size [2], density [3,4] and crystal morphology [5] play a role in the sensitivity of RDX. Recent investigations using scanning electron microscopy (SEM) [6–8], atomic force microscopy (AFM) [9,10], nuclear quadrapole resonance [11], UV/VIS optical absorption [12], Raman spectroscopy [13], small angle X-ray scattering and neutron scattering [14] have sought to quantify and/or link particular features to sensitivity.

There has been some speculation that certain surface properties of the RDX particles may contribute to its shock sensitivity. It has been reported that a secondary treatment of RDX particles to produce smoother surfaces has resulted in an increase of the required initiation pressure from 3.3 to 3.9 GPa [6]. Similarly, AFM analysis revealed that surface roughness parameters of RDX particles correlated with its shock sensitivity [10]. It has also been reported for 10–30 μm RDX particles that more shock sensitive particles had a greater surface roughness, measured using porosimetry, while for 100–300 μm particles no strong correlation between surface roughness and shock sensitivity existed [7].

In this study the relationship between the surface defects and their effect on the shock sensitivity of crystalline high explosives is investigated. Seven varieties of RDX having known characteristics such as impurity level, methods of manufacture, and shock sensitivity were examined. The specific varieties of the RDX materials studied were acquired from the previous Reduced-Sensitivity RDX Round Robin program [1]. There are two methods for the manufacture of RDX; Type I is produced by direct nitration known as the Woolwich process and Type II is produced by the acetic anhydride method known as the Bachman process. The major impurity in RDX is cyclotetramethylene-tetranitramine (HMX) and it has been reported to be as high as 17% [1]. The measure of shock sensitivity was determined through a large scale gap test and is the relative shock intensity required to produce detonation of the test sample 50% of the time. The test samples were prepared as a

* Corresponding author.
E-mail address: victor.bellitto@navy.mil (V.J. Bellitto).

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polymer-bonded explosive composition of 64% RDX, 20% aluminum, and 16% hydroxy-terminated polybutadiene (HTPB) binder [1]. The shock wave from the initiating charge before entering the test sample is attenuated by varied card thicknesses of poly(methylmethacrylate) (PMMA). The shock pressure entering the sample is determined from calibrations of the initiating charge-attenuating thickness system. A larger number of cards measured to achieve the 50% detonation translate to a smaller shock wave entering the sample and thus a more shock sensitive sample.

2. Experimental

AFM and advanced statistical analysis were employed to study the surface defects of the RDX high explosive materials. An example of an AFM image of the RDX particle surface is shown in Fig. 1. It represents the topography of an 1 μm $\times$ 1 μm scan. The dark circular features are voids inherent within the RDX. The edge dislocation observed along the white line between the cross-hairs was measured to be 1.4 nm. The types of defects and their density varied across different particles and sections of the same particle. Since the defects affect the crystallinity of the material and thus affect the surface roughness, the root mean square (RMS) of the surface topography was used to gauge the roughness.

The surface morphological images acquired in height mode were quantitatively compared using the RMS roughness calculation (R). The roughness is determined by finding the median surface height for the image and then evaluating the standard deviation of the image. The equation for calculating the surface roughness is

$$R = \sqrt{\frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1}[z(x_k, y_l) - \mu]^2},$$

where μ is the mean value of the height, z, across all in-plane coordinates (x,y):

$$\mu = \frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1} z(x_k, y_l).$$

The crystalline samples were attached to the AFM sample holder using double side tape. The images obtained were flattened using a first-order software algorithm provided by the Veeco Metrology Group. The flatten command is a filter that modifies the image to remove tilt and therefore levels or reorients the image.

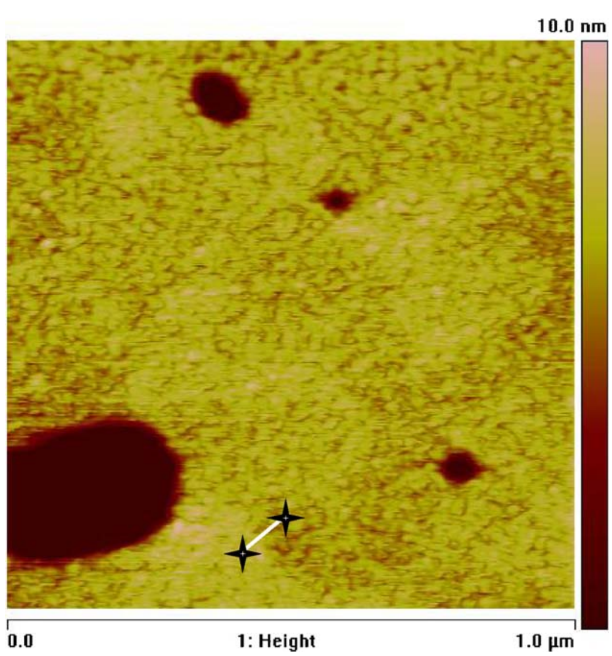

Fig. 1. AFM image of an RDX particle surface.

3. Results and discussion

Table 1 presents a basic summary of the seven materials used in our study. To investigate the surface characteristics, multiple particles for each material were studied and multiple scans of each particle were acquired. On average, 5–6 scans were obtained per particle and 5 particles for each material were used, resulting in a total number of scans of 190.

The multiple 1 μm scans of each particle surface provide a distribution of R (RMS) for each particle. To quantitatively measure the impact the surface characteristics have on the sensitivity of the material two characteristics of the surface roughness are quantified: the average value and its consistency across the surface. Both of these can be obtained statistically from the acquired samples.

The first of these characteristics is straight forward. For each particle (p) and material (m), the average measure of roughness, notated as $\bar{R}_{pm}$ is computed. Averaging these for each material provides the average value of the distribution of the mean,

$$R_m = \frac{1}{N}\sum_{p}\bar{R}_{pm},$$

which is an unbiased estimator for the average measure of surface roughness of material m.

The second characteristic is the consistency of the roughness across the surface of the material. To capture this characteristic of the material, given our sampling technique, two separate measures are constructed. One of these is a simple measure of variation in the roughness for each particle, the standard deviation (S_{pm}). From this the average variation of the particle is constructed for the material,

$$S_m = \frac{1}{N}\sum_{p} S_{pm}$$

as simply an arithmetic mean of the standard deviation of the particles for each material. This provides a method to quantify the average variation of the particle surface. The necessity to add objectivity to the consistency across the surface is demonstrated by Fig. 2. Although the two AFM scan images obtained are from the same particle of material D (Dyno Nobel type II) they show two very different surface features and have different roughness measurements of 2.94 and 9.28 nm.

Also, since these particles represent samples of the material, variation across particles is also likely and is seen in the distribution of the mean. To capture this variation an additional variable, the standard deviation for the mean distribution is constructed.

Table 1
Manufacturer, grade, type, % HMX impurity and shock sensitivity measurements for each material.

Material	Manufacturer	Grade	Type	Impurity % HMX	Sensitivity (GPa)
A	Ordnance Systems Inc.	RDX	II	7.36	4.2
B	Eurenco	I-RDX	I	0.02	4.66
C	Eurenco	MI-RDX	I	0.03	2.21
D	Dyno Nobel	Type II	II	8.55	3.86
E	Dyno Nobel	RS-RDX	II	0.82	5.24
F	ADI	Grade A	I	0.02	5.21
G	Royal Ordnance Defence	Grade A	I	0.19	5.06