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## **DUAL ADVANTAGES OF ULTRAFINE CRYSTAL-SIZED ENERGETIC/REACTIVE MATERIAL FORMULATIONS**

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### **ABSTRACT**

Evidence is presented for greater mechanical insensitivities and greater energy release rates being achieved for explosive and propellant formulations designed with smaller particle sizes.

### **INTRODUCTION**

High explosives, such as RDX (cyclotrimethylenetrinitramine,  $[\text{CH}_2 \text{ N NO}_2]_3$ ), HMX (cyclotetramethylenetetranitramine,  $[\text{CH}_2 \text{ N NO}_2]_4$ ), and PETN (pentaerythritol tetranitrate,  $\text{C}[\text{CH}_2 \text{ N NO}_2]_4$ ) are known for their relative insensitivity to initiation by mechanical forces but, once initiated, these same energetic materials are known for their high explosive power. Considerations relating to both properties are principally involved in the engineered use of the materials in munitions and propellants.

#### **Enhanced Mechanical Insensitivity: Greater Strength**

The initiation of RDX and related materials by mechanical forces and deformations, at least, up to low-shock loading rates, has been attributed to the localized development of hot spots of critical sizes and temperatures. In turn, the needed temperature rise at any mechanically-induced hot spot has been attributed to thermal conversion of the plastic work that is substantial once plastic straining commences. Thus, the consideration of greater plastic resistance, that is associated with a greater strength level of the material, leads in turn to a greater insensitivity to imposed

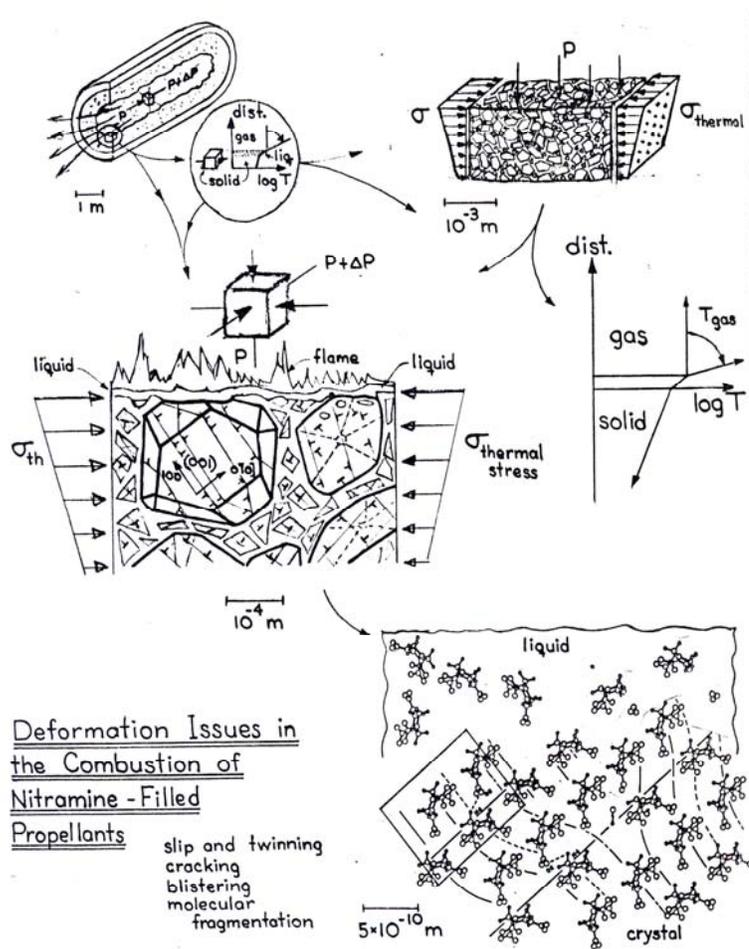
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Key Words: RDX, HMX, mechanical insensitivity, energy release rates, dislocations, crystals, hardness, impact, combustion, granular compaction, shock loading

mechanical forces. And, an important method of strengthening materials is to refine their grain sizes, when in polycrystalline form, or to refine their crystal sizes if they are to be brought into mutual contact by mechanical loading, say, as occurs for impact of crystal piles or during granular compaction.

### Enhanced Energy Release Rate: Greater Power

Chemical reactions/decompositions are known to be enhanced at external or internal material surfaces or at interfaces or other defect structures. The decomposition products of the high explosives are gaseous species that are more

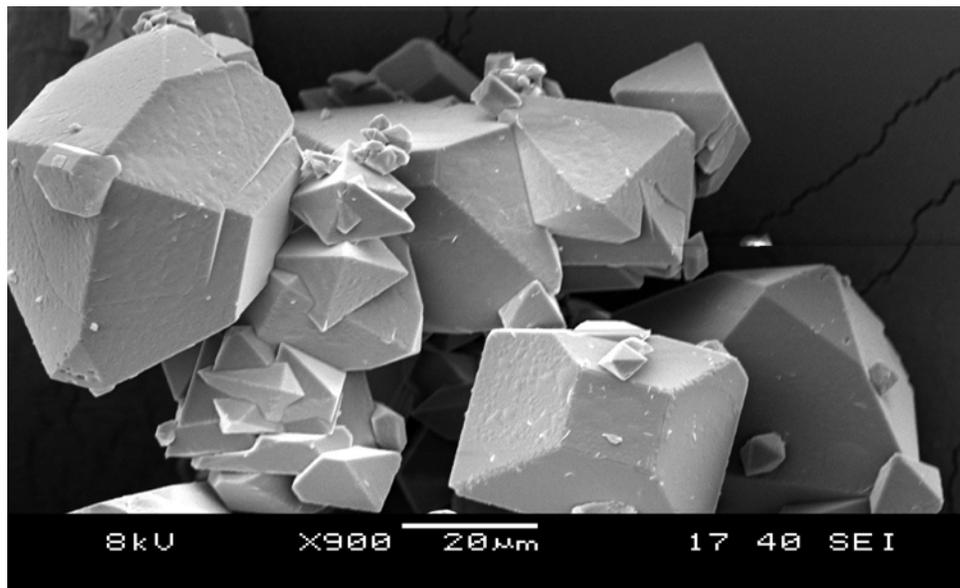


**Figure 1.** Deformation-connected macro-to-nano-structural aspects of propellant combustion: Pressure and thermal gradients, internal stresses between the viscoelastic and viscoplastic composite constituents, and dislocation structures.<sup>1</sup>

easily liberated at, or near to, free surfaces. Also, particulate aluminum is an important constituent of many energetic material composite formulations; and, the energy released by oxidation is achieved at the particle surface through Al atoms diffusing outward at rates that are slow compared to explosive reaction times. Such combined considerations lead to an enhancement of overall energy release rates being achieved for the greater surface-areas-to-volumes of smaller particles. An indication of the complexities involved in the combustion of an energetic propellant formulation is shown in Figure 1, covering a wide range in dimensional scale and where burning takes place over a liquid layer. At the micrometer-to-millimeter scale shown at the flame surface for the composite formulation depicted in Figure 1, indication is given of the action of thermal straining on causing plastic flow in a polygonal-shaped crystal, for example, of RDX. Dislocations, represented by inverted "T"s, are shown within slip bands traversing the crystal cross-section. Micro-cracking caused by such thermal straining has been proposed to generate an increased sensitivity to pressure.<sup>2</sup> A section view is given of an adjacent crystal whereby its internal growth sectors, growth sector boundaries, and grown-in dislocations are revealed.<sup>3</sup> At the lower-right corner of the Figure, an (002) projection of the RDX unit cell is shown as the rectangular box and adjacent to it are the schematic positions of RDX molecules in the core region of a [100] Burgers vector dislocation positioned on the (040) slip plane.

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## STRUCTURAL CHARACTERIZATIONS



**Figure 2.** A scanning electron micrograph of RDX recrystallized from solution.<sup>4</sup>

## **Crystal Morphologies and Sizes**

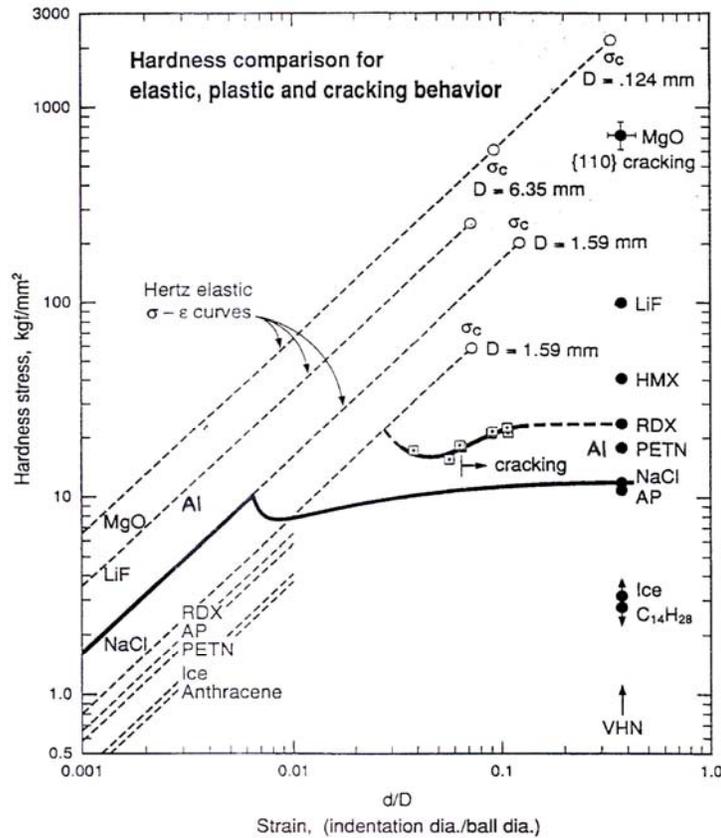
The orthorhombic RDX unit cell structure is reflected in the geometrical arrangement of the external surface planes forming the polygonal crystal growth morphologies. Such crystal growth surfaces are crystallographically identifiable, for example, in Figure 2, where the tabular crystal in the lower-right corner exhibits {111} pyramidal surfaces capped by a top flat (001) surface that, incidentally, is the easiest cleavage plane for RDX.<sup>3</sup> Perhaps more interestingly, in the top-left corner of the Figure, the larger crystal is seen to contain near to its top (001) surface a twist-type fault produced by partial rotation about the [001] surface normal. In addition, a new smaller crystal is seen to have been grown onto the top of the mismatched corner structure formed by the offset edge intersections of the two pairs of adjacent {111} planar surfaces. Such external crystal evidences relate to the presence of dislocation defects that play an important role, along with the crystal anisotropic surface energies, in determining a variety of crystal morphologies and sizes under different growth conditions applied to various solvent solutions.

## **Dislocation Structures**

The internal growth sectors with growth sector boundaries and dislocation bundles, as mentioned for Figure 1, have been identified for RDX also.<sup>3</sup> X-ray Laue diffraction patterns and topographic images from different crystals have revealed different internal strains that are relatively magnified for such molecular crystals because of the large nm-scale Burgers vectors of the dislocations. A variety of dislocation Burgers vectors are obtained, presumably, because of the weak bonding between the irregularly-shaped molecules. However, in agreement with experiment, a comparison of the dislocation self-energies and crystal surface energies leads to expectation of relatively low dislocation densities being generated during crystal growth. Model consideration of dislocation movements leads to the expectation of relatively strong resistance to their motion, again in agreement with experimental observations.

## **CRYSTAL HARDNESS PROPERTIES**

Based on experimental and model descriptions of molecular bonding and dislocation characteristics, the individual crystals of RDX, HMX, PETN and related materials are: elastically, relatively compliant; plastically, relatively hard; and, fracture-wise, relatively brittle.<sup>3</sup> The combination of mechanical properties is well illustrated by the comparison of theoretical and experimental hardness stress-strain behaviors shown for various energetic and inert materials in Figure 3, including Al.<sup>1</sup>

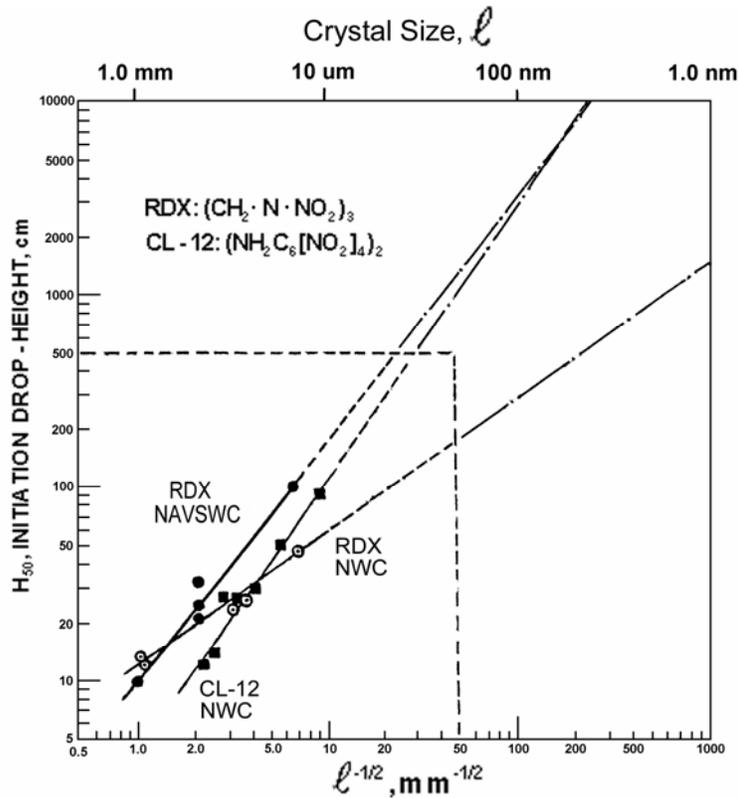


**Figure 3.** Energetic and ionic crystal hardnesses on an indentation stress-strain basis.

Beginning in the lower-left corner of Figure 3, the stiffer ionic bonding, say, of NaCl produces a raised Hertzian linear elastic behavior compared to RDX that however has a greater hardness because of the difficulty of dislocation movement. The same comparison applies for PETN and HMX. Also, the relative brittleness of RDX is shown by the lower theoretical elastic cracking stress,  $\sigma_c$ , when indented with a 1.59 mm steel ball, compared to that for NaCl. Such cracking stress is lower for a larger ball diameter, as shown for MgO at two ball sizes. Cracking is shown to have occurred at the plastic indentations in RDX at lesser hardness values than  $\sigma_c$  because of the stress concentrating action of dislocation pile-up stresses.<sup>5</sup> On the other hand, whereas evaluation of indentation fracture mechanics measurements of the stress intensities required for crack growth in RDX shows that plastic flow is extremely limited at crack tips, such plastic flow apparently controls the actual mechanisms of crack growth.

## IMPACT DYNAMICS

The relatively small stress range for RDX between its measured hardness values and the corresponding  $\sigma_c$  value in Figure 3 is interpreted to mean that few dislocations are required in pile-ups to initiate cracking and also that only a small range in (hardness) stress is available for increasing the plastic flow stress by dynamic loading. Such loading in drop-weight impact tests is well-known as a conventional method of assessing the impact sensitivities of explosive crystal piles and their solid formulations. And, Figure 4 shows the crystal size dependence for  $H_{50}$  designated as the drop-weight height for 50% probability of initiation.<sup>3</sup>



**Figure 4.** Initiation drop-weight height dependence on crystal size.

In Figure 4, the experimental results following a linear log-log dependence of  $H_{50}$  on inverse square root of crystal size,  $\ell^{-1/2}$ , are in agreement with a dislocation model description for hot spots proposed to be generated at pile-up avalanches released at crack initiation points.<sup>3</sup> Of current interest in Figure 4 is the enlargement of the graph from the previous dashed framework so as to consider the extrapolation of the crystal

insensitivity results to nanometric dimensions at which encouraging experimental results have been obtained.<sup>6,7</sup>

## COMBUSTION

An advantageous particle size influence at nanometric dimensions on enhancement of the burning rate of Al/ammonium perchlorate (AP) strands and, at two particle sizes, Al within a higher pressure gun propellant is shown in Figure 5. Also, the Al/AP burn rate dependence on pressure is shown at the 200 nm particle size, yielding an unstable burn rate of ~500 mm/s at 15 MPa.

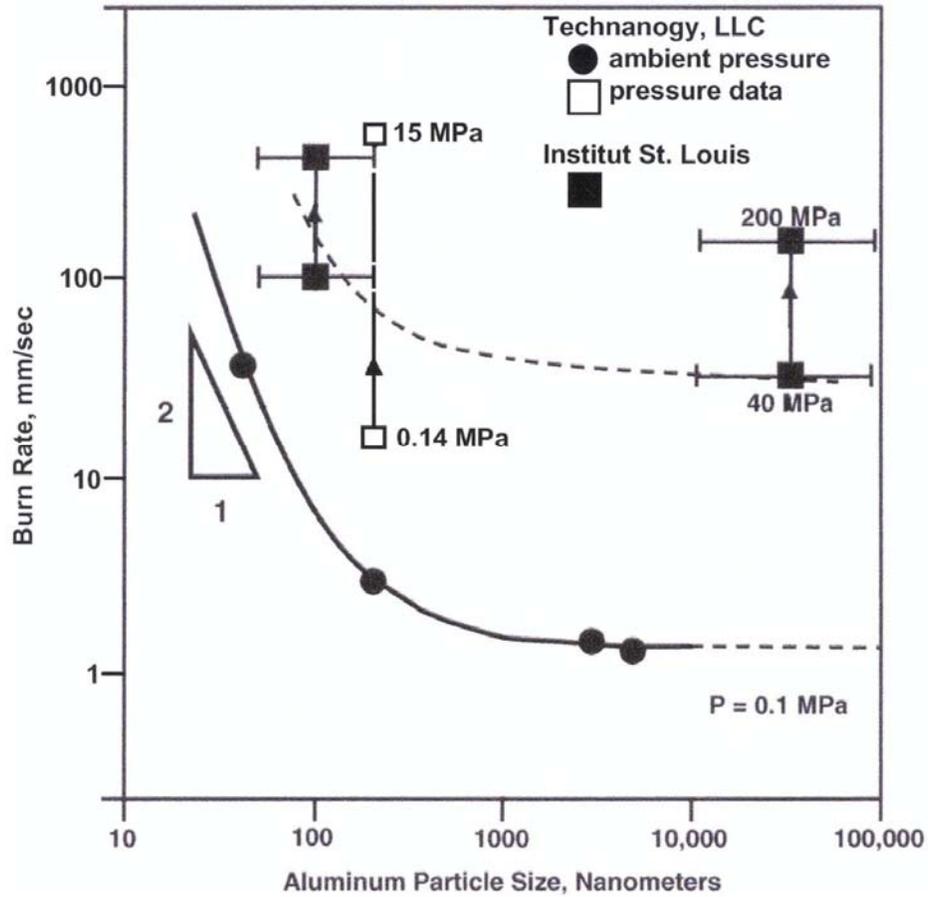
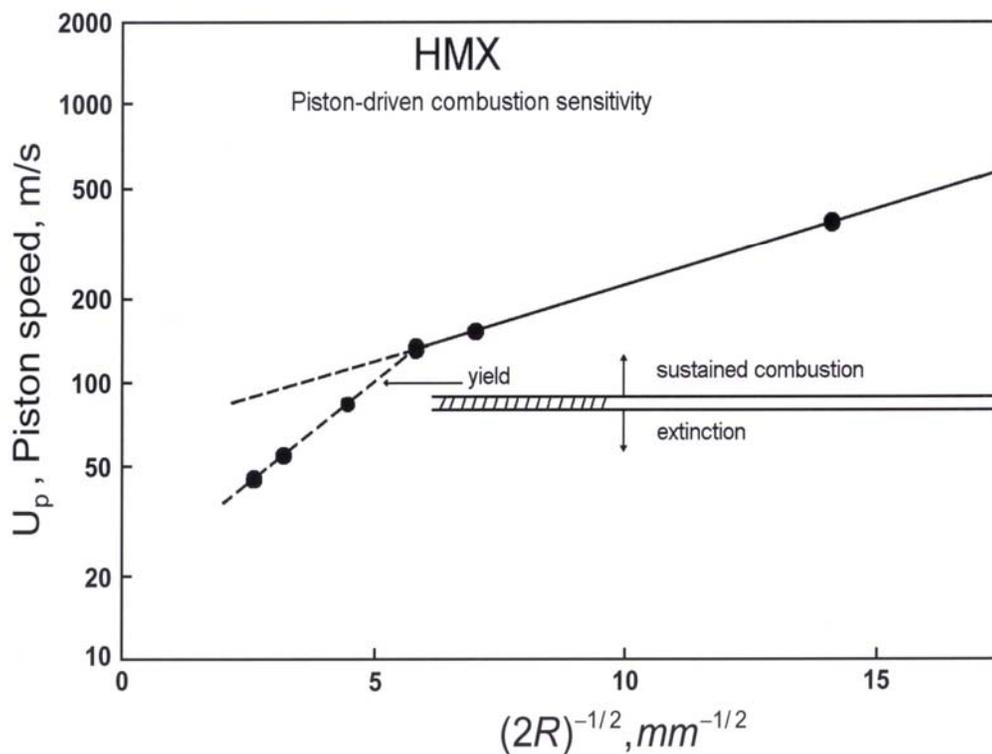


Figure 5. Burn rate dependence on Al particle sizes

The measurement details for Figure 5 are reported elsewhere.<sup>8</sup> The results follow on from similar measurements that were reported earlier.<sup>9</sup> Here, attention is directed to the inverse square of the particle size dependence, or inverse surface area dependence, for the burn rate at the 10's of nm scale.

In addition to such direct burn rate measurements under pressure, study of the initiation of combustion during the granular compaction of particles is important for practical and research interest, for example, relating to the role of hot spot development. Figure 6 shows an example of the modeled role of HMX particle radius,  $R$ , on the compacting piston velocity required for sustained combustion.



**Figure 6.** Piston speed vs inverse square root of particle radius for combustion.

The Figure is adapted from results<sup>10</sup> reported for the correlation of combustion and plastic yield propagation from particle-to-particle based on an analysis of the Hertzian contact stresses developed during compaction, for example, as described for Figure 3. The inverse square root of particle size dependence is taken to relate to that shown also for the drop-weight impact properties depicted in Figure 4. At reasonably high compaction densities, particle cracking becomes important. Specification of the combustion conditions relates to the so-called deflagration-to-detonation transition (DDT) behavior that is to be avoided for particulate composite propellants.<sup>1</sup> Crystal

melting and molecular fragmentation occur during thermal stress development as propellant combustion proceeds under thermal pressure fluctuations and combustion products venting in a full-sized rocket motor, as schematically characterized at the top of Figure 1. The complex phenomena are modeled with hydrocode computations.<sup>11,12</sup>

## **SHOCK LOADING BEHAVIORS**

Great importance is attached to particle size influences on detonation induced by shock wave loading. The shock front is modeled hydrodynamically to involve discontinuities of pressure, temperature, and density across an idealized shock front of nm-scale width. At low shock pressures, smaller particles are less sensitive to initiation<sup>13</sup> --- and the same hot spot explanation applies as given for the impact behavior. At high shock wave pressures, the situation is reversed and small particles are initiated more easily --- and one explanation given for the behavior concerns the growth of reaction to detonation being faster for the smaller particles.<sup>14</sup> Other explanation possibly may be tracked to the rather special dislocation considerations that obtain for shock wave loading.<sup>15</sup> First, and foremost, is the consideration that the very significant strains capable of being imposed at all points of a shock front are not able to be relaxed by the relatively remote movement of a residual dislocation density. Consequently, at sufficient shock pressures, a nanoscale network of dislocations is sequentially created at the shock front and left behind to interact with the lagging movement of the originally resident dislocation structure. Of course, at the greatest shock pressures, initiation is proposed to occur within the strain field cores of the resident dislocation structure. The topic is currently of great research interest because of focus on the nanometric characteristics of a variety of proposed mechanisms that lend themselves to research challenges both for instrumentation diagnostics<sup>16</sup> and molecular dynamics modeling.<sup>17</sup>

## **CONCLUSIONS**

On crystal structure and dislocation model bases, the crystal hardness properties, impact dynamics, combustion, granular compaction, and shock loading behaviors of energetic materials give strong indication that improvements in explosive and propellant formulations are to be achieved with designed reductions in the constituent particle sizes.

## **ACKNOWLEDGMENT**

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