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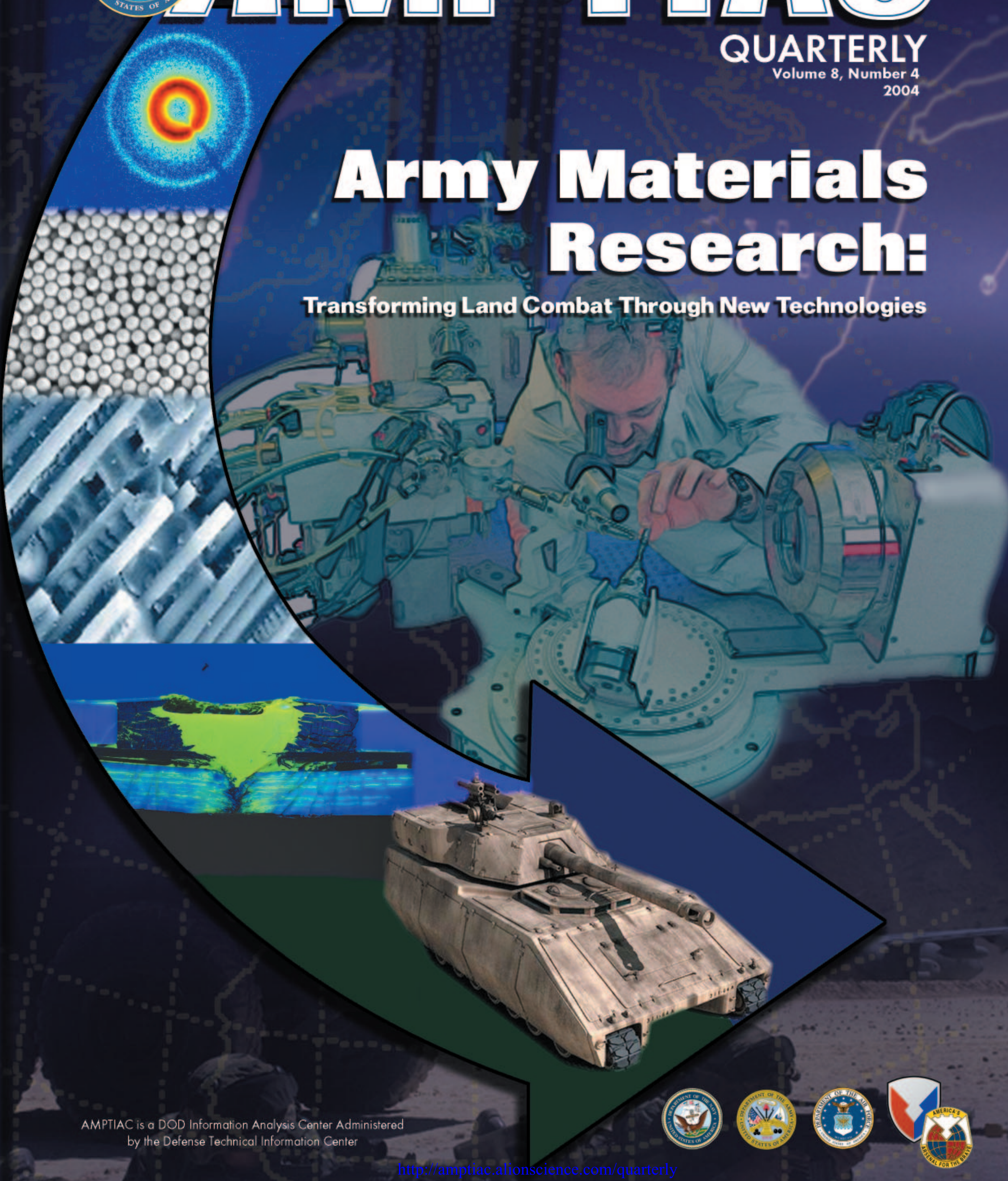
Army Materials Research:

Transforming Land Combat Through New Technologies



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Editorial: Adapting to a Changing Battlefield

Regular readers of the *AMPTIAC Quarterly* will have noticed that we've published several 'special issues' over the past few years. The common aim of these publications has been to highlight topics of special interest to targeted technological communities. Examples include our issues on nanotechnology (May 2002) and blast mitigation (*Protecting People at Risk*, February 2003). Both issues were well received by our readers but for different reasons: Nanotechnology represents an exciting and unexplored frontier with intense scientific interest; while protecting people and structures from explosions has gained national attention, especially since 9/11. This current issue addresses perhaps an even more important topic: the development of new technologies to enable our ground troops to become more effective in the war against terror as well as other emerging global threats.

All one has to do is follow the news reports to appreciate the major technological hurdles now facing the Army. Gone are the days when we faced large standing armies, consisting of heavily armored units employing traditional tactics much like our own. Today, we face adversaries that seemingly have no qualms at sacrificing their lives or those of innocent bystanders in an attempt to inflict damage on our troops. Through a mix of conventional and unconventional weapons (such as improvised explosive devices or IEDs) these fanatics have forced us to adopt new tactics while relying upon our existing weaponry and equipment.

To be totally effective against our new and other possible future enemies, the Army must transform from a force relying on heavy armor to one employing a broad spectrum of lightweight, yet survivable systems and equipment that will enhance their ability to fight. In this context, the word 'transform' means to change doctrine, tactics, and assets to respond rapidly to the environments of the new battlefield. The challenge for our community is to develop the advanced materials that will provide the Army improved effectiveness across the full spectrum of operational environments. To make things even more complex, researchers must address additional 21st Century requirements beyond mere system performance. They must give greater consideration for 'green' solutions that reduce the generation or introduction of toxic materials into the environment during production, training, deployment, or other military operations.

Much recent work has been undertaken to improve the survivability of vehicles and their occupants subjected to fire from ballistic weapons as well as blast and fragmentation from mines, Rocket-Propelled Grenades (RPGs), and IEDs. Discussed in this publication are several of the emerging materials that will enable improved yet lighter armor for future systems. Included are ceramic, metal, and composite material research programs that show tremendous promise. Past armor research has yielded the effective but heavy systems we employ today. Becoming more effective against insurgents requires lighter armored vehicles employing innovative materials including transparent armor for windshields and visors. Armor research has been and continues to be a significant activity at the Army Research Laboratory.

Other subjects of significant interest are those related to ordnance materials, including propellants, projectiles, and even the systems used to shoot them. One area of concern lately has been to find replacements for lead bullets and depleted uranium (DU) kinetic energy penetrators. Environmental concerns are the primary reasons for finding alternative materials for these applications, and several of the articles here discuss the programs addressing the problem.

One approach to reduce the weight and complexity of systems is to develop multifunctional materials that perform two or more primary functions. Army researchers have many programs underway that are leading to technologies that exploit this concept and several of them are mentioned here. A multitude of other technology development efforts are also being examined to develop the new generation of lighter, higher performance materials needed to improve warfighting effectiveness.

The twenty separate articles contained in this issue of the *AMPTIAC Quarterly* will provide you with a glimpse at some of the technologies that will enable the Army to transform into a more mobile, survivable, and lethal force while simultaneously becoming a better steward of the environment. There are numerous technical challenges yet to be overcome, but as the reader will notice the Army Research Laboratory's Weapons and Materials Research Directorate (ARL/WMRD) is actively pursing those technologies necessary for the Army to transform the face of the new battlefield.

David H. Rose
AMPTIAC Director

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Novel Energetic Materials for the Future Force:

The Army Pursues the Next Generation of Propellants and Explosives

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INTRODUCTION

The changing nature of international conflicts requires the development of new war-fighting capabilities within the Department of Defense. It is recognized by the US technology community that advanced energetic materials with substantially enhanced performance, reduced sensitivity, and controlled (or manageable) energy release will be critical enablers for precision weapons. In the past ten years revolutionary breakthroughs in munitions technology were made through aggressive development of advanced energetics by the worldwide community.

Much of the synthesis effort over the past 50 years has been directed toward compounds that contain only carbon, hydrogen, nitrogen, and oxygen (CHNO explosives). For most of the past 40 years the benchmark against which high energy CHNO ingredients have been compared was cyclotetramethylenetetranitramine (HMX).

In 1987, a new compound, hexanitrohexaazaisowurtzitane (CL-20) was synthesized for the first time by the Navy. It is more energetic than HMX and does not have most of the instabilities of other high energy compounds that have precluded their use. The traditional procedure for formulating new materials such as CL-20 has been largely guided by intuition, experience, and testing, relying heavily on trial and error. The ever-increasing need for rapid deployment of emerging weapons systems dictate a streamlining of the development process of advanced high-energy insensitive materials tailored for optimal performance in advanced weapons.

Developments in computational chemistry and physics based modeling using High-Performance Computing (HPC), chemical synthesis and formulation, and materials science are providing the key factors that will provide breakthroughs in the performance of energetic materials. The DOD HPC network and advanced modeling science and technologies afford a critical means to rapidly close the technology gap and expedite the design and prediction of new revolutionary advanced energetic materials (Figure 1).

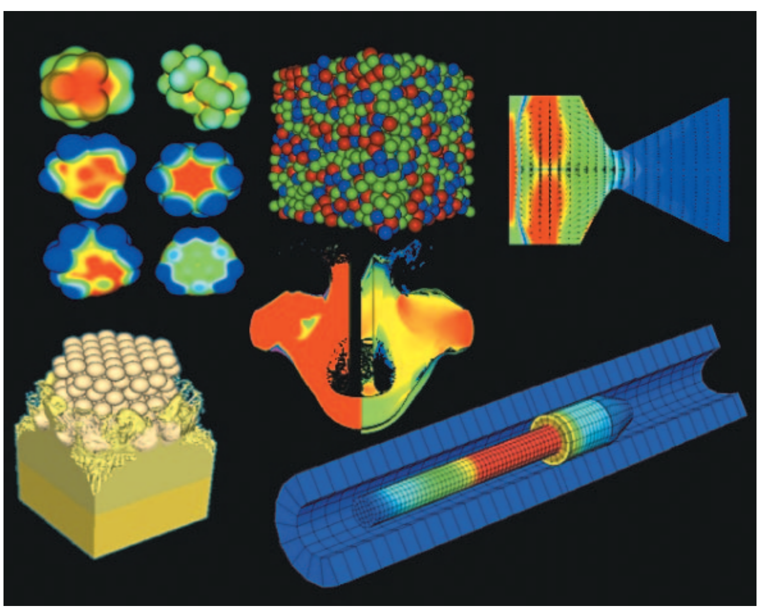

Figure 1. **High-Performance Computing Modeling and Simulation of Energetic Materials and Advanced Propulsion.**

ADVANCED GUN PROPELLANT MATERIALS

The Army initiated a significant effort in the design, formulation, and fabrication of future insensitive high-energy materials for Future Force weapons and is extensively leveraging science and technology from the national energetics community. A key objective is to develop advanced gun propellants having high energy release, increased burning rates, improved mechanical and environmental properties using nanomaterials and other novel high energy ingredients, while ensuring compliance with insensitive munitions requirements. The reduction in carbon content is also favorable as it reduces degradation and wear of steel gun barrels. Recent

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work in synthesis and characterization of new novel energetic materials has centered on the following energetic materials:

- Nano-particulates (metals, crystalline solid organics)
- Metal hydrides
- CHNO and CHNOF compounds
- All-nitrogen species
- High-nitrogen species
- Boron containing compounds (e.g., carboranes)
- Energetic liquids with potential as monopropellants

Gun propellants in layered disk geometries are of interest for applications in which an outer, slower burning layer is sandwiched with a center, faster burning layer to produce what commonly is referred to as "fast-core" propellant using chemical progressivity. The advantage of the fast-core concept is that at times early in the ballistic cycle before the projectile has moved significantly, a lower volume of gas is generated by the slower burning layer, so that pressures do not exceed the maximum pressure sustainable by the gun system. However, once the projectile begins to move and the volume available for expansion of the propellant gases increases, the inner, faster-burning core provides a greater level of gas to maintain work against the projectile for improved performance over that achievable with a uniformly-burning material. In practice, with energetic materials currently available, realization of this concept requires charge designs for which aspect ratios (length/diameter) are an order of magnitude less than in conventional charges and the individual layers are nominally 2-3 mm thick. This makes the mechanical properties requirements much more stringent than for colayered propellants.

Figure 2. Advanced Gun Propellant Formulations with Energetic Nanomaterial Ingredients.

High Nitrogen Compounds

High nitrogen compounds, including azo-tetrazolates, dinitramide salts, tetrazine derivatives, amino-azo-furazans, guanidine salts and diazido-nitrazapentane, have been investigated as burning rate modifiers for energetic formulations. Formulations using high nitrogen compounds have increased the burning rate differential to 3:1 between inner and outer colayered formulations required for performance improvements by chemical progressivity. Additionally, these formulations result in lower gas temperatures during expansion into high flow areas and increased ratio of nitrogen to carbon monoxide in the combustion products, compared to conventional propellants. Thus, wear and erosivity is reduced, increasing gun barrel lifetimes by reducing the dissociation of carbon monoxide and subsequent adsorption/absorption of carbon into the steel barrel [1].

New Energetic Binder Components

Energetic thermoplastic elastomers (ETPEs) are being considered for a wide range of applications, including binders for large caliber gun propellants. In addition to the fact that they can be processed without the use of solvents that pose health problems, they also offer potential performance improvements in weapon systems. The oxetane chemistry has been the basis for the polymer backbone, to which energetic pendant groups have been attached, including nitro, nitrate ester, nitramine, and in particular, the azide group. The ETPEs enable compositions with different energetic crystals to be readily processed into a stable layered geometry with good adhesion and without problems associated with plasticized propellants, such as diffusion between layers of different compositions, and oxidizer migration to and crystallization on the outer surface. The azido-ETPE polymers are of particular interest because of potential for high burning rates afforded by the azide group, and also the higher nitrogen content has been shown to help reduce the adverse effects of gun erosion.

Plasma Ignition Technologies

Electrothermal-chemical (ETC) and electrothermal ignition (ETI) gun technology is an advanced gun propulsion concept that utilizes both chemical and electrical energy for initiation of high-energy, high-loading density propellants to provide increased performance, lethality, and range. ETC gun propulsion technology utilizes electrical energy to form a high-temperature, high-energy plasma that augments the control and release of chemical energy stored in advanced high-performance propellants, in order to achieve significant performance enhancements over existing conventional guns. ETC technology offers many advantages over conventional gun propulsion including:

- An ability to tailor the pressure (thrust) of the propulsion gases of the chemical reaction through the electrically generated superheated plasma and propellant gases, resulting in increased projectile range or reduced acceleration-loading on the projectiles.

- An extremely reproducible ignition, providing precise and predictable muzzle velocities and gun tube dynamics, culminating in increased ordnance on target and less ordnance required to achieve a given hit probability, and gun recoil mitigation.

Nanoenergetic Materials

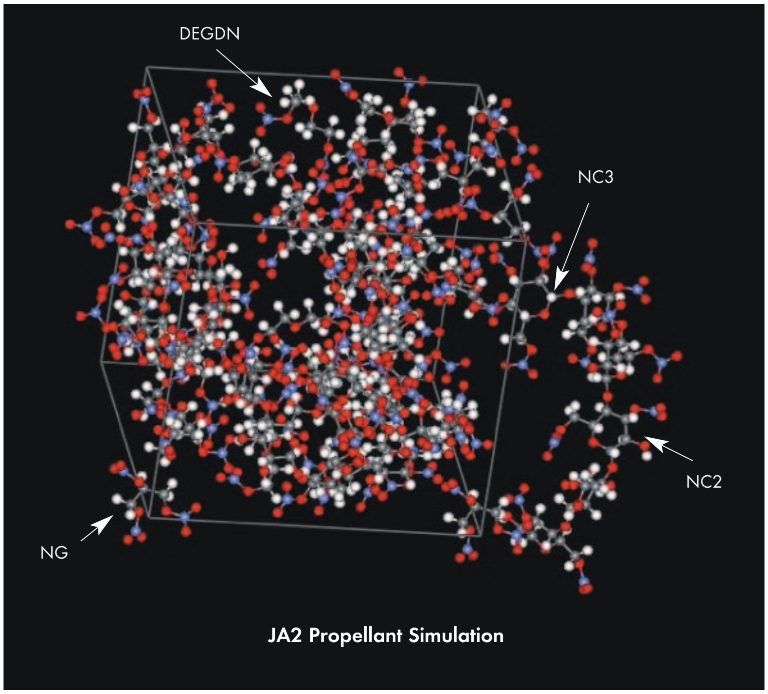
Energetic nanomaterials offer the potential of extremely high heat release rates, extraordinary combustion efficiency, tailored burning rate, and reduced sensitivity. However, exploiting these possibilities requires an understanding of: (a) properties of the individual nanoscale material, (b) the interaction of the nanomaterial with the matrix; (c) the interface behavior of the nanomaterial and the matrix; (d) energy release and dynamics of combustion and initiation processes on such short length scales (e) high-rate synthesis and practical scale-up of nanomaterials. Nanoscale energetic materials are currently being exploited to improve the combustion efficiency of advanced gun propellants, Figure 2.

Nanometals

The primary nanometals being considered for energetic material applications are aluminum and boron. Aluminum has long been an important burn rate accelerator for rocket propellants, especially in the nanoparticle form. The hope is that burning rate promotion obtained at modest pressures in rocket propellants will be realized for the high pressure regime of gun propellants. An oxide coating naturally forms on aluminum which detracts the energy available to the system. Ultra-high resolution microscopy techniques have enabled the imaging of an oxide surface 2.5 nm thick, mainly amorphous, but with crystalline layers which appear to exfoliate[2,3].

Prompt gamma neutron activation analysis has revealed greater levels of hydrogen and water present in nano-aluminum than for flake aluminum, which could enable porosity. Additional elements, which may also modify the initiation and energy release of aluminum, have been detected in nano-aluminum by X-ray Photoelectron Spectroscopy. In fact, since manufacture of nano-aluminum relies on recrystallization and quenching of aluminum from the high temperature plasma condition, doping of the bulk aluminum and/or oxide surface offers a tool for tailoring the atomic scale structure of nanometals.

Boron hydride compounds demonstrated great potential as burning rate accelerators, but spontaneous ignition of these materials rendered them too hazardous for practical application. Recently, ARL produced the ability to synthesize boron-based nanoparticles [4]. Future efforts will address coating particles of boron with other energetic materials which offers promise for taking advantage of the high heat of combustion and potential for burning rate promotion of nanoboron.



(DEGDN – Diethylene Glycol Dinitrate, NG – Nitroglycerin)

Figure 3. **The First Molecular Model of JA2 Advanced Gun Propellant.**

Extended Carbon Structures

Extended carbon structures, such as carbon nanotubes (CNTs) are being investigated for application to controlled performance (through burning rate modification and the increased energy of strained structures), and improved insensitivity (by encapsulation to control particle size and to buffer the effects of accidentally applied stimuli). The structure of CNTs gives them unique properties, including high thermal and electrical conductivity, and a very high aspect ratio, since their diameters are nanoscale while their lengths can be micro-scale. Their high conductivities and aspect ratio make them attractive candidates for serving as a type of "mini-fuze" distributed throughout energetic materials, yielding the potential for burning rate and combustion tailoring with very little parasitic mass.

Through the use of carbon nanotubes it may also be feasible to enhance the specificity of a propellant formulation to initiation due to the high electron density and conductance localized on the nanotube walls. Moreover, because of their unique structure, they may be used for confining energetic molecules in a nano-matrix with a positive effect on sensitivity properties.

Nano-Crystalline Energetic Materials

Anti-solvent recrystallization techniques, in both the liquid and supercritical phases, as well as rapid expansion of supercritical solutions, are being used for preparing nanocrystals of energetic oxidizers. Ultimately the goal is to prepare ultrafine particles with tunable particle size and morphology as well as a uniform size distribution. Crystals with fewer voids and uniform morphology are expected to yield decreased sensitivity results through the reduction of sites for possible hot spot formation that can lead to energetic material initiation. Nanocrystals of energetic compounds including, but not limited to cyclotrimetylenetrinitramine (RDX) and CL20 have been prepared and characterized [5]. Although optimization of process-

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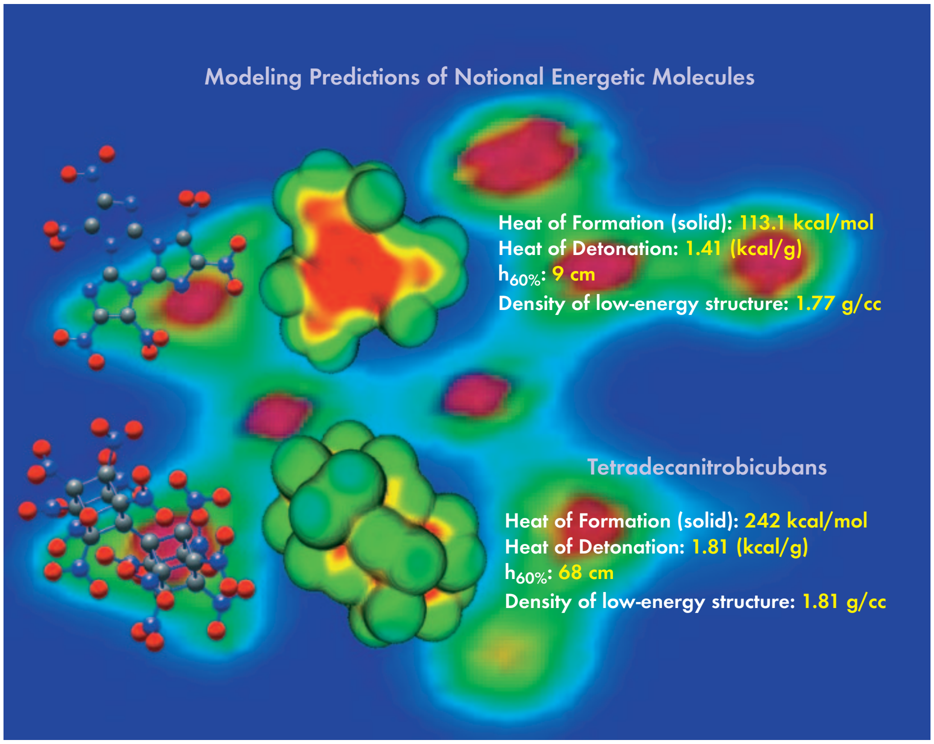

Figure 4. Theoretical Chemistry Predictions of Novel Energetic Molecular Properties.

ing variables of the various techniques is ongoing, preliminary characterization of the products generally show fewer irregularities and lower void content.

Smart Design of Energetic Materials Using Theoretical Chemistry

An accurate and reliable predictive capability can provide the information and insight needed for the intelligent design of energetic materials. The refinement and implementation of key computational chemistry methods are being used in a model-based design process for new energetic materials to achieve a process for atomistic model-based screening of notional materials. Included are methods that involve quantum mechanical predictions of properties of isolated and condensed phase explosives that are related to their performance and vulnerability. Other methods involve the utilization of intermolecular interaction potential energy functions that can be used in molecular simulation to explore the response of a material to initiation events. The methods and software are being developed within the Army Research Laboratory mission program and in conjunction with the DOD HPC Modernization Common High Performance Computing Scalable Software Initiative to provide an automatic and seamless set of procedures for the simulation and screening of potential energetic materials. In addition, molecular models are being developed to predict chemical and physical properties of propellant formulations such as JA2 used in 120 mm tank ammunition, Figure 3.

Quantum Mechanical Predictions of Properties of Notional Materials Associated with Performance or Sensitivity

Computational tools have been developed that are based on quantum mechanical calculations that describe relationships between the quantum mechanical properties of an isolated molecule and its behavior on the macroscale [6-8]. The predictive methods all use quantum mechanical predictions of the electrostatic potential that surrounds an isolated molecule. The first two computational tools that were developed have reasonably predicted Heats of Formation [6] and Detonation [7] for a large variety of CHNO explosives. The most recent application of quantum mechanical predictions of isolated molecules has shown that the electrostatic potentials for surfaces of equal electron densities surrounding CHNO explosive molecules are useful guides in assessing the degree of sensitivity of a CHNO explosive [8].

Crystal Structure/Density Prediction Using Molecular Packing

The property of solid-state density, required to assess accurately the ideal performance of gun propellants in current interior ballistics calculations, is not obtained from computer calculations but rather from known experimental values. The reliance on external sources for something as important as density is, of course, an unacceptable situation for a practical and widely applicable modeling system. A procedure for the prediction of possible crystal structures for an unknown compound has been developed [9], which accounts for factors such as the structure and conformation of a molecule, probable crystal packing arrangements and packing efficiency. The so-called "model-MOLPAK-WMIN" procedure consists of three steps: (1) construction of a reasonable three-dimensional model for the compound of interest (the search probe) followed by ab initio quantum mechanical geometry optimization; (2) determination of a number of possible crystal structures for the search probe (MOLPAK program); (3) refinement of the unit cell parameters (WMIN program[10]), search probe orientation and position by lattice energy minimization for the best of the crystal structures derived in Step 2, using a model function to describe interatomic interactions. The model being employed has been shown to reproduce the crystallographic parameters of over 80 crystalline systems, whose molecules contain functional groups common to explosives [11]. The suite of molecular simulation tools are now being employed to a priori predict properties on notional (new) candidate energetic materials, Figure 4.

SUMMARY

Novel energetic materials hold the promise of providing the following payoffs: (1) mission-enabling lethality at range by enhanced lethality and effectiveness and (2) crew survivability under ambush for the full range of Future Force weapons. The increased energy and efficiency of new energetic materials concepts will enable increased lethality through additional propulsion energy or impulse on the target. Alternatively, the same amount of energy as delivered by existing systems could be delivered to the target using less energetic material or a multipurpose energetic material, thus minimizing logistics burdens.

Decreased sensitivity of energetic materials will significantly reduce platform vulnerability. By managing the energy release of specific systems, it will be possible to maximize ballistic efficiency in advanced gun systems while also increasing the performance of compact rockets/missiles. In addition, it may be possible to minimize collateral damage with the use of powerful precision strike weapons against hard targets or targets surrounded by noncombatants, and also maximize effectiveness against soft yet distributed targets by spreading impulse and heat over time and distance. Finally, it seems reasonable that these new energetic materials may enable novel and efficient methods for eliminating incoming threat munitions, or they could be utilized as multi-purpose energetics (e.g. to provide thrust and/or detonate on target).

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