A Unified Multiscale Approach for Nano-Engineered Energetic Materials-NEEM MURI

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Objectives

- To develop new methodologies for synthesis and assembly of nano-engineered energetic materials (NEEMs).
- To obtain fundamental understanding of the relationship between the structures of NEEMs and their reactive and mechanical behavior, particularly with regard to sensitivity, ignition, burning characteristics, mechanical properties, and optimum loading density, thus enabling design optimization of NEEMs.

Approach

The program makes use of a combination of (1) novel nanotechnology fabrication techniques, in particular, molecular self-assembly and supramolecular chemistry for synthesizing and assembling energetic materials, (2) state-of-the-art theoretical modeling techniques that can interrogate events occurring from the atomistic/molecular scale through the mesoscale to the macroscale, and (3) experimental diagnostic techniques that can capture the reactive dynamics at femtosecond timescales to those that evaluate overall combustion performance.

Relevance to Army

Historically, it is well known, although not well understood, that a strong correlation exists between the energy density of an energetic material and its sensitivity. The successful development of NEEMs may provide the means to unravel and control this relationship. The program outcome will help enable DoD to fabricate molecularly designed energetic materials at the nano-scale with tuned chemical and physical properties that yield improved performance and reduced sensitivity, and the possibility of multi-functionality.

Accomplishments for Reporting Period

- Energetic nanocomposites have been made by coating 50 nm diameter Al particles with 1-10 nm Fe, Ru, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au nanoparticles. High resolution microscopy shows that the nanocomposites do not have a core-shell structure, but instead have a papular morphology.
- Boron nanoparticles have been surface-functionalized for the first time. TGA studies show that surface functionalization can improve storage properties but maintain high energy release.
ALEX® nano-sized aluminum particles have been successfully coated with RDX through a modified RESS system. This was confirmed by characterization of the recovered particles including field emission scanning electron microscope (FE-SEM) images.

From sensitivity tests of RESS synthesized nano RDX vs. military grade RDX at NAVSEA Indian Head facility, it has been determined that nano RDX synthesized at PSU is much less sensitive to impact (H50=44 cm) compared to military grade RDX (H50=17 cm).

The laser ignition of a variety of nanoparticle composites consisting of 50 nm Al particles, either in a neat thin film, or with oxidizers nitrocellulose and teflon and with inert polybutadiene has been studied using an improved flash-heating emission spectroscopy apparatus. These materials have been studied as a function of laser ignition pulse energy and particle concentration.

The thermal response of self-assembled monolayers on metal surfaces has been studied using a flash-heating technique combined with ultrafast nonlinear coherent vibrational spectroscopy.

A laser-driven flyer plate apparatus has been developed. It consists of a launch laser with a state of the art beam shaper to produce top hat beams, a microfabricated laser flyer plate array, and a variety of high speed diagnostics to monitor flyer plate launch including a fast imaging system and an 8 GHz displacement interferometer. Flyer plates 0.8 mm in dia. have been launched having velocities up to 4 km/s.

Reaction pathways of nascent Al atoms, prepared by controlled vapor deposition, with different oxidizer molecules arranged in well-organized self-assembled monolayer (SAM) arrays on support surfaces have been studied using in-situ Infrared Reflection Spectroscopy (IRS), X-ray photoelectron spectroscopy (XPS) and Atomic Force Microscopy (AFM) in ultra high vacuum (UHV) chambers. Results show that even bare, highly reactive Al atoms at near ambient temperatures have to overcome a large kinetic energy barrier to drive highly exothermic product formation. In contrast, only simple Al-O-N-M bonds appeared to form, leaving the major molecular and NO2 bonding nearly intact. Results also indicate that even SAMs with a second oxidizing functional group do little to increase the overall reactivity of the molecule towards Al atoms.

Experiments have been performed that involve the deposition of potassium metal on top of nitro containing SAMs. It is well known that potassium will readily give up its 4s1 electron to a nitro functional group to form K+ and the NO2 radical anion. By first priming the SAM with a partial layer of potassium metal, studies were performed to see if the 1-electron injection would lower the reaction barrier to full reaction between Al and the NO2 functional group and achieve the thermodynamically expected reaction products.

High level DFT calculations on a model system consisting of an eight nitrobenzene thiol molecule monolayer subunit have been performed in an effort to better understand the interaction between the aluminum metal atoms and the nitro SAM surface. Future plans include examining the effect of a potassium atom on the complexation of Al on the nitro SAM surface. These data then will be related to the chemistry of clusters such as Al13K, which has been developed by Prof. W. Castleman at PSU under ARO MURI support.

Measurements of the reaction temperature for the Al/CuO system were made using a multi-wavelength pyrometry. The results show that the reaction temperature is below the vaporization temperature of Cu and Al and consequently, the gas that is formed from the reaction is likely from the decomposition of CuO yielding molecular and atomic oxygen as intermediates in the overall reaction.

The reaction propagation through nano-scale aluminum and nickel powders in small tubes. Propagation velocities near 1 cm/s were measured, which is considerably slower than the nAl thermites. Packing density has been found to have only a minor effect on the rate of propagation. Nano foils of aluminum and nickel have been fabricated and complementary cold spray materials are understudy.
• Mulimillion-atom MD simulations have been performed for slow burning aluminum nanoparticles (ANPs) in oxygen and an onset temperature (~740 °C) at which self-heating begins was determined. The simulation results reveal a two-stage reaction mechanism involving confined and spallation phases. Initiation is focused in hot spot areas, which develop at the inner boundary of alumina shell and aluminum core. Resulting increase in oxygen mobility provides energetically favorable migration of oxygen into aluminum core. The oxygen diffusion at the internal boundary is the primary mechanism of energy release in the first reaction phase, leading to local temperature extremes along the shell.

• Divide-and-conquer DFT (DC-DFT) based MD simulations have been performed to study thermite reactions at an Al/Fe₂O₃ interface. The results reveal a concerted metal-oxygen flip mechanism that significantly enhances the rate of redox reactions. This mechanism leads to two-stage reactions—rapid initial reaction due to collective metal-oxygen flips followed by slower reaction based on uncorrelated diffusive motions, which may explain recent experimental observations in thermite nanowire arrays. The 1152-atom DC-DFT MD simulation for 5 ps (6000 MD time steps) took 985 hours on 960 (3.2 GHz Intel Xeon) processors.

• A general framework has been developed capable of handling nickel-aluminum interactions for the study of thermodynamic behavior of nickel-coated aluminum particles. The model has been benchmarked against the phase transition of bulk nickel and bulk aluminum.

Collaborations and Technology Transfer
• At Penn State, Yetter has continued collaborating with personnel (Dr. Tim Foley and Dr. Blaine Asay) at LANL and Prof. Steve Son at Purdue University. Eden and Yetter at PSU have also been collaborating with Matthew Trexler at the Army Research Laboratory on cold spray of reactive materials and combustion analysis. Kuo and his team members communicated with Dr. Brad Forch, Dr. Joe Colburn, Dr. Bill Anderson, Dr. Jeff Morris, and many other scientists at the Army Research Laboratory about nano-sized RDX particle synthesis using the RESS technique. Dr. Suhithi Peiris of DTRA was also informed about the advancements of RDX coating on aluminum particles. In addition, Kuo and his graduate student Timothy Wawiernia visited Dr. Ruth Doherty and Mr. Dan Remmer of NSWC-IHD in March 2008 to conduct a collaborative test program at Indian Head in order to perform sensitivity testing of the recovered nano-sized RDX particles. These tests were performed in July 2008. Allara and Yetter have been collaborating on depositing layer by layer intermetallic structures and measuring the heat release as a function of the multilayer structure. Allara and Dlott have been collaborating on ultra fast thermal propagation in SAMs. Allara and the USC group have collaborated on DFT/MD calculations.

• At USC, the atomistic understanding gained from this project will lead to the development of new and improved materials and structures with enhanced energy density and reduced sensitivity for a wide range of DoD applications, by significantly accelerating the pace of experimental research and through our extensive collaborations with DoD scientists (Dr. William Wilson at DTRA; joint paper “multimillion atom reactive simulations of nanostructured energetic materials” in Journal of Propulsion and Power with Dr. Barrie Homan and Dr. Kevin McNesby at ARL; our students’ internships with Dr. Betsy Rice and Dr. Margaret Hurley at ARL; and mutual visits by Dr. Brad Forch and Dr. Shashi Karna at ARL). The USC dual-degree students (Ph.D. in the physical sciences or engineering with MS in Computer Science specialized in High Performance Computing and Simulations) have continued to do internships with DoD collaborators.

• At UIUC, Dlott has discussed his research extensively with collaborators at the DOE labs LAN, LLNL, and Argonne. He has also discussed simulations of self-assembled monolayers with Vashishta at USC, and spectroscopy of fluorocarbon-coated nanoparticles with Dr. Jason
Jouet of NSWC. In an extension of the aluminum nanoparticle work, Girolami has collaborated with UES, Inc., to develop new methods to coat steel parts with aluminum to improve their corrosion resistance.

**Resulting Journal Publications During Reporting Period**

RESS System,” accepted for presentation at the 8th International Symposium on Special Topics of Chemical Propulsion, Cape Town, South Africa, November 2-6, 2009.


Graduate Students Involved During Reporting Period

Richard Clark, USC, Weiqiang Wang, USC, Rusty Conner, UIUC, Chuck Spicer, UIUC, Brian Bellott, UIUC, Yuanxi Fu, UIUC, Jeffrey A. Carter, UIUC, Kathryn E. Brown, UIUC, Puneesh Puri, PSU/GIT, Dilip Srinivas Sundaram, PSU/GIT, Mike Weismiller, PSU, Justin Sabourin, PSU, Steven Dean, PSU, Andrew C. Cortopassi, PSU, Jonathan T. Essel, PSU

Awards, Honors and Appointments


Dlott became the Lycan Professor of Chemistry and Jeffrey A. Carter received a Merck Fellowship in Analytical or Physical Chemistry

Allara was elected Fellow of the Royal Society of Chemistry (UK), 2009.

Yang received the Propellants and Combustion Award in 2009 from the American Institute of Aeronautics and Astronautics

Kuo received the 2009 AIAA Pendray Aerospace Literature Award from AIAA in January of 2009. Kuo also received a citation plaque from NAVSEA-Indian Head for achievement in Combustion and Propulsion at the 2009 National Capital Region Energetics Symposium held in La Plata, MD on April 27-28, 2009 and in July 2009, the DOTC and NWEC presented an award to Kuo with the
following statement: “In Grateful Appreciation of his Service and Commitment to the Success and Growth of the DoD Ordnance Technology Consortium.”
Objective
The goal of this project is to develop new methodologies for synthesis and assembly of nano-structured energetic materials. The scientific challenges include
- Can self-assembly methods afford energetic nanoparticles that are stable against environmental degradation?
- Can one make energetic aluminum and boron nanoparticles by a bottom-up approach?

Approach
- Use bottom-up rather than top-down approaches to synthesize energetic nanoparticles
- Investigate self-assembled monolayers (SAMs) as surface passivating agents to increase stability of nanoparticles to environmental degradation.
- Increase energy density by developing chemical methods to make boron nanoparticles
- Investigate soft lithographic methods and hierarchical nanoparticle structures to generate intimate fuel-oxidizer interfaces
- Passivate aluminum nanoparticles with sacrificial transition metal monolayers

Relevance to Army
Successful development of new and advanced explosives and propellants with higher energy densities, controlled energy release rates, increased storage lifetimes, and reduced handling hazards.

Accomplishments for Reporting Period
- Energetic nanocomposites have been made by coating 50 nm diameter Al particles with 1-10 nm Fe, Ru, Rh, Ir, Ni, Pd, Pt, Cu, Ag, and Au nanoparticles.
- High resolution microscopy shows that the nanocomposites do not have a core-shell structure, but instead have a papular morphology.
- Boron nanoparticles have been surface-functionalized for the first time. TGA studies show that surface functionalization can improve storage properties but maintain high energy release.
Collaborations and Technology Transfer

- In an extension of the aluminum nanoparticle work, Girolami has collaborated with UES, Inc., to develop new methods to coat steel parts with aluminum to improve their corrosion resistance. UES, Inc., based in Dayton, Ohio, is a science and technology company that commercializes technology breakthroughs into products and services, in the areas of material science and processing, metallurgy, computer science, physics, aerospace power and propulsion technologies, environmental science, toxicology, biotechnology, and nanotechnology.

Resulting Journal Publications During Reporting Period


Graduate Students Involved During Reporting Period

- Chuck Spicer (Ph.D., graduated in 2008)
- Brian Bellott (Ph.D., current)

Awards, Honors and Appointments

- Ralph G. Nuzzo was elected a Fellow of the American Vacuum Society, 2007
- Gregory S. Girolami was elected a Fellow of the American Association for the Advancement of Science, 2007
Equation 1: Synthesis of aluminum nanoparticles via the reduction of alane ethyldimethylamine adduct using titanium(IV) isopropoxide as the catalyst.
Figure 1: Powder X-ray diffraction of as-synthesized aluminum nanoparticles. The peaks at $2\theta = 38.5$, $44.7$, and $65.1^\circ$ are indicative of aluminum.
Equation 2: The reaction with metal acetylacetonate salts with aluminum nanoparticles gives aluminum nanoparticles coated with smaller transition metal nanoparticles.
Figure 2: Representative images of aluminum nanoparticles coated with smaller transition metal nanoparticles. Left: aluminum nanoparticles coated with ruthenium nanoparticles. Middle: aluminum nanoparticles coated with copper nanoparticles. Right: aluminum nanoparticles coated with nickel nanoparticles.
Figure 3: Two images obtained on the Jeol 2200 Cs corrected microscope. The image on the left shows a well ordered Pt nanoparticle supported on the aluminum nanoparticle (color-coded vertical height shows that the particle is spherical). The image on the right is another Pt nanoparticle with a non-spherical shape.
Equation 3: The reaction of aluminum nanoparticles with SiCl$_4$ followed by reduction of Pt(acac)$_2$ by the previously synthesized particle gives aluminum nanoparticles passivated by an adlayer of platinum atoms.
A Unified Multiscale Approach for Nano-Engineered Energetic Materials-NEEM MURI

Professor Kenneth K. Kuo
Department of Mechanical and Nuclear Engineering
The Pennsylvania State University, University Park, PA, 16802

Objective
The overall objective of this study is to use the Rapid Expansion of a Supercritical Solution (RESS) process to coat nano-sized aluminium particles and to continue to synthesize nano-sized RDX particles. The scientific questions to be answered include: 1) Can nano-sized aluminium particles be efficiently coated through the RESS process? 2) What coating thickness can be achieved from varying the temperature and pressure of the process along with the aluminium particle concentration? 3) What are the performance characteristics of the coated particles in regards to ignition temperature and ageing characteristics?

Approach
- Develop and test a high-pressure RESS system with controlled temperature and pressure to rapidly expand a supercritical solution with entrained nano-sized aluminum particles
- Confirm that the nano-sized aluminum particles have been coated by RDX through scanning electron microscope (SEM) characterization
- Optimize the operating conditions along with the aluminum feeding rate to achieve uniform coatings of aluminum particles
- Characterize particle coating thickness, ignition performance, and ageing characteristics of the coated nano-sized aluminum particles

Relevance to the Army
The benefits and relevance to the Army include a potentially new energetic material synthesized in an efficient way. This new material could have better performance characteristics than a bulk mixture of nano-sized aluminium particles and RDX. The material should have greater resistance to forming a thick alumina shell on the outer layer of the aluminum particle, and should be much easier to ignite than uncoated nano-sized aluminium particles. Using a continuous RESS process to coat the nano-sized aluminum particles should be more efficient than other methods. The high-pressure RESS system can also be utilized to coat other energetic materials than nano-sized aluminium particles. This system can also be scaled up for producing large quantities of energetic nano-sized coated aluminium particles required by the U.S. Army.

Accomplishments for Reporting Period
- Modification of the ultra-high pressure RESS system to introduce ALEX® particles into the supercritical solution this included:
1. Designing and fabricating an entrainment vessel with an aluminum particle holder to introduce ALEX® particles into the supercritical fluid.
2. Demonstrated the proper entrainment of ALEX® particles to flow through expansion nozzles in the RESS system.
   • Successfully coated ALEX® nano-sized aluminum particles with RDX through the modified RESS system. This was confirmed by characterization of the recovered particles including field emission scanning electron microscope (FE-SEM) images.
   • From the sensitivity tests of RESS synthesized nano RDX vs. military grade RDX at Indian Head facility, it has been determined that nano RDX synthesized at PSU is much less sensitive to impact (H₅₀=44 cm) compared to military grade RDX (H₅₀=17 cm). These results have been summarized in technical papers prepared for journal publication.

Collaborations and Technology Transfer
• Professor Kenneth Kuo and his team members communicated with Dr. Brad Forch, Dr. Joe Colburn, Dr. Bill Anderson, Dr. Jeff Morris, and many other scientists at the Army Research Lab about the nano-sized RDX particle synthesis using the RESS technique. This work was also presented at the National Capital Region Energetics Symposium organized by NSWC-Indian Head in La Plata, MD in April, 2009. Dr. Suhithi Peiris of DTRA was also informed about the advancements of RDX coating on aluminum particles.
• Professor Kenneth Kuo and his graduate student Timothy Wawiernia visited Dr. Ruth Doherty and Mr. Dan Remmer of NSWC-IHD in March 2008 to conduct a collaborative test program at Indian Head in order to perform sensitivity testing of the recovered nano-sized RDX particles. These tests were performed in July 2008. The joint technical paper is being submitted for publication in the International Journal of Energetic Materials and Chemical Propulsion.

Resulting Journal Publications During Reporting Period

Graduate Students Involved During Reporting Period
• Andrew C. Cortopassi (M.S. conferred and currently for a Ph.D.)
• Jonathan T. Essel (Ph.D., current)
Awards, Honors and Appointment

- Prof. Kenneth Kuo received the 2009 AIAA Pendray Aerospace Literature Award from American Institute of Aeronautics and Astronautics (AIAA) in January of 2009.
- Prof. Kenneth Kuo received a citation plaque from NAVSEA-Indian Head for achievement in Combustion and Propulsion at the 2009 National Capital Region Energetics Symposium held in La Plata, MD on April 27-28, 2009.
- In July 2009, the DOTC and NWEC presented an award to Professor Kuo with the following statement: “In Grateful Appreciation of his Service and Commitment to the Success and Growth of the DoD Ordnance Technology Consortium.”

Additional Information

Table 1: RDX Sensitivity Testing Results Conducted Under Collaboration Between PSU and NSWC-IHD

<table>
<thead>
<tr>
<th>Particle Sample</th>
<th>ERL Impact Test $H_{50}$ [cm]</th>
<th>ABL Friction Test 20 TIL [psig]</th>
<th>ABL ESD Test 20 TIL [J]</th>
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</thead>
<tbody>
<tr>
<td>Nano RDX</td>
<td>44</td>
<td>100</td>
<td>0.165</td>
</tr>
<tr>
<td>RDX Standard</td>
<td>17</td>
<td>135</td>
<td>0.165</td>
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</table>
Figure 1: a) Process flow diagram for modified ultra-high pressure RESS system, b) Photograph of Aluminum Entrainment Vessel
Figure 2: Phase diagram of CO$_2$ and conjectured path in the RESS process for coating ALEX$^\circledR$ particles

Figure 3: Block diagram showing the three-step RESS process for coating ALEX$^\circledR$ particles
Figure 4: FE-SEM images of ALEX particles and RDX coated ALEX® particles: (a)-(c) ALEX® powder, 35,000 magnification

(d)-(f) RDX coated ALEX® powder, 35,000 magnification
A Unified Multiscale Approach for Nano-Engineered Energetic Materials-NEEM MURI

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Objective
The goal of this MURI project is to study nano-structured engineered energetic materials (NEEMs), using large (billion atoms) multiscale simulations that couple quantum-mechanical (QM) calculations to molecular dynamics (MD) calculations. We calculate stability, structure and energetics of metallic nanoparticles with a special focus on the relationships between particle size, shape and excess surface free energy. Multiscale modeling of the thermo-mechanical properties and microscopic mechanisms of detonation and deflagration processes of NEEMs is performed.

Approach
We use our adaptive hierarchical quantum mechanical (QM)/molecular dynamics (MD) simulation framework, which invokes higher accuracy simulations only when and where high fidelity is required. We have developed scalable parallel QM and MD simulation algorithms, with which we have benchmarked unprecedented scales of quantum-mechanically accurate and well validated, chemically reactive atomistic simulations—1.72 billion-atom reactive MD and 19.2 million-atom (1.68 trillion grid points) QM simulation in the framework of the density functional theory—in addition to 218 billion-atom non-reactive MD, with parallel efficiency well over 0.95 on 212,992 CPUs. We also perform multimillion-to-multibillion atom MD simulations in house at USC on our 2,048-CPU Opteron cluster.

Relevance to Army
Atomistic understanding of shear-induced initiation will lead to the prediction of material properties prior to the experimental synthesis of nano-reactive materials, so that safety and survivability will be increased with enhanced performance.

Accomplishments for Reporting Period
Fundamental understanding and precise control of reaction rates and initiation time are of critical importance for nanostructured energetic materials. However, the reactivity of nanoenergetic materials is known to differ drastically from their micron-scale counterparts. For example, experimental studies on the combustion of nanothermites, such as Al/Fe$_2$O$_3$ and Al/MoO$_3$, have shown that flame propagation speeds approach km/s when the size of Al nanoparticles is reduced to below 100 nm, in contrast to cm/s for traditional thermites. Another example is the two-stage reaction of Al/CuO-nanowire thermite, in which the first reaction takes place at 500 °C followed by the second reaction at 660 °C (i.e., Al melting temperature). Such peculiar reactive behaviors of nanothermites cannot be explained by conventional mechanisms based on mass diffusion of reactants, and thus various alternative mechanisms have been proposed. An example is a mechanochemical mechanism that explains the fast flame propagation based on dispersion of the molten metal core of each nanoparticle and spallation of the oxide shell covering the metal core. Another mechanism is accelerated mass transport of both oxygen and metal atoms due to the large pressure gradient between the metal core and the oxide shell of each metal nanoparticle. In addition, defect-mediated giant diffusivity is important for fast reactions at the nanometer scale.

Burning of Aluminum Nanoparticle by Slow Heating
We have performed multimillion-atom MD simulations of slower burning ANPs in oxygen and found the onset temperature (~740 °C) at which self-heating begins. The simulation results reveal a two-stage reaction mechanism involving confined and spallation phases. Initiation is focused in hot spot areas, which develop at the inner boundary of alumina shell and aluminum core. Resulting increase in oxygen mobility provides energetically favorable migration of oxygen into aluminum core. The oxygen diffusion at the internal boundary is the primary mechanism of energy release in the first reaction phase, leading to local temperature extremes along the shell.
Simulation results show a transition to a second reaction mechanism approximately 90 ns after initial reaction. Localized heating at the shell internal boundary and development of oxygen-poor regions lead to shell weakening. Resulting shell failure leads to spallation of small aluminum clusters into surrounding oxygen, generating additional heat by direct oxidation. Mechanism of reaction in both stages and identification of transition point are confirmed via fragment analysis, radial composition/temperature analysis, and statistical particle migration calculations.

The detonation of ANPs is a complex phenomena which results from the interaction of several mechanisms taking place on scales which range from the atomic interactions of individual chemically-reacting atoms (~angstroms) to the feature size of the total particle (5-10 nanometers). In the small scale, the creation of hotspots and the oxidation of spallated fragments contribute to the initiation and detonation phases of the reaction. On the larger scales, the mechanical breaking of the shell, phase changes within the component materials, and internal pressures which develop throughout the detonation also are expected to contribute to the overall behavior. As the overall evolution of the particle itself is a combination of these mechanisms, it is impossible to gain a comprehensive view of the controlling factors of detonation without being able to look at both scales simultaneously. In the previous simulations, we examined the role of non-uniform heating in the detonation response by looking at ANP systems, which were given the same energy in a uniform manner. Although this is very useful in analyzing the effect of laser-initiation on particle detonation, it does not provide a ready comparison to experiments performed on heated systems due to the extreme energy scales at work. To this end, we performed a multi-million atom MD simulations, which studied a particle being heated to a more conventional temperature (just above the melting point of aluminum) to accomplish the following objectives:

1. Analyze the burning of ANPs in order to better understand the mechanisms, which control its evolution.
2. Identify the key components of the initiation and burning of the ANP, which must be included in any coarser simulations that seek to properly capture its behavior on a larger scale.
3. Provide a contrast study to the laser-initiated simulation results, allowing comparison of the two initiation methods.

Several mechanisms leading to initiation in ANP materials have been presented in the scientific literature over the last decade. One predominant mechanism proposed by Pantoya, Levitas, et al. for burning is that the particle remains stable until the core temperature exceeds the melting temperature of bulk aluminum ($T_m = 933$ K). At this point, the phase change from solid to liquid in the core (with the associated 12% volume increase) results in a considerable pressure buildup on the inner boundary of the shell. This pressure is enough to mechanically fracture the shell barrier, resulting in the spallation of unoxidized aluminum clusters into the surrounding oxidizer. The direct oxidation of these clusters is said to generate a large temperature increase, resulting in the complete burning of the particle and surrounding material.

In contrast to these findings, the primary mechanism leading to burning in this simulation appears to rely on the chemical oxidation of the core at the core-shell boundary prior to shell failure. The increase in the particle’s temperature creates additional mobility of oxygen atoms at the inner shell boundary, resulting in a migration of oxygen into the core. As the oxygen penetrates from the previously stable shell inward, the resulting exothermic reactions locally increase the temperature of the core-shell interface, resulting in a runaway reaction, which sustains itself until the particle reaches several thousand degrees (and total shell failure). This mechanism is summarized in Fig 1.

Detailed results, analysis, and interpretation of the MD simulation are shown below in order to understand fully the above model. We first identify the stages of reaction by looking through the overall picture of the burning process. As indicated above, the complexity of the ANP burning and detonation behaviors make them difficult to analyze and describe without first breaking down the fundamental components into their respective parts. To this end, the particle evolution is divided into two stages of burn following initiation: confined burning and spallating burning. Each of these phases relies on a different set of internal mechanisms, which govern the reaction behavior. As such, each phase can be identified by changes in the rate of heat production within the system as a whole. The temperature of the particle is presented in Fig. 2(a), and the rate of temperature change (i.e., heat production) is presented as Fig. 2(b). It is apparent in the above that a dramatic change in the rate of heat production occurs at 80-90 ps. This will be shown in the following to be the transition from the confined burning phase to the spallating burning phase (referred to as “Stage 1” and “Stage 2”, respectively).

The burning of the ANP during Stage 1 is governed by oxidation of core aluminum atoms by penetrating oxygen from the shell. In the following graph, the temperature of the particle at multiple time steps is graphed as a function of its radius (Fig. 3). It shows that from $t = 0$ ps, the highest temperature region is located at the core-shell boundary. Also, by the increase in temperature over time, it is apparent that the heat generated at the core-shell boundary is building faster than the thermal transport throughout the rest of the particle, resulting in the formation of a much high interface at the internal boundary than in the rest of the particle.
Second, in the fragment analysis of the ANP for the first 130 ps (Fig. 4), it can be seen that the aluminum-rich fragments (left side of the graph) steadily increase (as the penetrating oxygen partially oxidizes the core atoms). The sudden boom of aluminum-poor fragments (light blue bar) occurs later, after the particle has transitioned into Stage 2. From this, it can be reasoned that the bulk of the early reactions are occurring at the inner boundary of the shell, rather than on its exterior.

A third, more direct, method to detect the movement of oxygen atoms into the core can be accomplished by performing analysis on the shell as a whole. If we define the shell as all atoms that are connected (via Al-O bonds) to the largest fragment in the particle, it is possible to isolate the shell from the rest of the system. The inner radius of this entity shows the movement of oxygen into the core, expanding the shell in an inward direction. Despite the overall expansion of the particle, the area claimed by the shell is seen to deepen considerably over time (Fig. 5).

Finally, the movement of atoms as a whole can be viewed by rendering a slice of the ANP at two time steps. In the following images, the core aluminum atoms have been hidden to show the migration of the oxygen into the core region. It can be seen that although the particle itself remains approximately the same size, a large influx of oxygen has been pulled into the inner regions.

The reaction’s stage 2, the spallating burning stage, was identified in the heat-produced graph (Fig. 2(b)) as occurring at approximately 80-90 ps. At this point, a fundamental change in the mechanism of heat production occurs within the particle, resulting in a dip in this graph (though the temperature itself continues to increase—Fig. 2(a)). The change at this point can be seen most readily in the graph of the aluminum present outside the shell boundary (as defined above). This change is highlighted by the red arrow in Fig. 7.

From the above, it is apparent that the onset of stage 2 is connected with a sudden increase in the number of ejected aluminum atoms from the shell surface. These small clusters enter the surrounding oxygen, and are quickly oxidized. This change is accompanied by a matching change in the increase of oxygen-rich fragments in the system, seen in Fig. 8.

During stage 2, the particle continues to be heated by both the oxygen penetration and the aluminum ejections until the temperature plateau seen in Fig. 2(a) is reached. At this point, the oxygen has completely penetrated the particle core, seen in Figs. 9 (a) and (b).

The above analysis demonstrates the importance of the inner core-shell boundary in the burning of the ANP. Unlike the laser-initiated detonation case (where the shell was fractured and ejected away from the particle upon initiation), in the heating case the shell has plenty of time to greatly contribute to the burning process. This leads us to the conclusion that the core and the shell cannot be treated as two isolated pieces which interact only via the internal pressure. Instead, they must be considered as a chemically reacting combination.

Enhanced Reactivity of Nanothermite

We have also performed divide-and-conquer DFT (DC-DFT) based MD simulations to study thermite reaction at an Al/Fe₂O₃ interface. The results reveal a concerted metal-oxygen flip mechanism that significantly enhances the rate of redox reactions. This mechanism leads to two-stage reactions—rapid initial reaction due to collective metal-oxygen flips followed by slower reaction based on uncorrelated diffusive motions, which may explain recent experimental observation in thermite nanowire arrays mentioned above. The 1152-atom DC-DFT MD simulation for 5 ps (6000 MD time steps) took 985 hours on 960 (3.2 GHz Intel Xeon) processors.

We have simulated a stack of Al and Fe₂O₃ layers involving 1152 (144 Fe₂O₃ + 432 Al) atoms in an orthorhombic supercell with dimensions \((L_x, L_y, L_z) = (20.1 \text{ Å}, 26.2 \text{ Å}, 28.2 \text{ Å})\) with periodic boundary conditions. The hematite (Fe₂O₃) crystal, cut along (0001) planes to expose Fe planes, is placed in the supercell with the (0001) direction parallel to the \(z\) direction. The Fe planes of the hematite are attached to (111) planes of the face-centered cubic Al crystal at the two interfaces. Our DC-DFT method iteratively minimizes the energy functional using a preconditioned conjugate-gradient method to determine electronic wave functions. The grid spacing \(\sim 0.25 \text{ Å}\) (corresponding to the cutoff energy of 45 Ry in the plane wave-based method) for the real-space representation of the wave functions is sufficiently small to obtain a good convergence of the total energy. We use a norm-conserving pseudopotentials and a generalized gradient approximation for the exchange-correlation energy. The DC-DFT method divides the system into 960 \((= 8 \times 10 \times 12)\) domains of dimensions \(2.51 \times 2.62 \times 2.35 \text{ Å}\). Figure 10 shows the side \((yz)\) view of the non-overlapping cores of the domains in the supercell. Each domain is augmented with a buffer layer of depth \(= 2.2 \text{ Å}\) to avoid boundary effects. The interatomic forces thus computed quantum-mechanically are used to integrate Newton’s equations of motion numerically (with a time step of 0.84 fs) in MD simulations to study atomic motions and chemical reactions. The MD simulations are carried out at temperature 2000 K in the canonical ensemble.
Snapshots of the atomic configuration are shown in Fig. 10, where the side (yz) views of atomic configuration are displayed. We observe that the oxygen atoms in hematite migrate into the aluminum metal to form aluminum oxide and leaves behind liquid iron. Our DC-DFT simulation thus describes complete thermite reaction, \( \text{2Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} \).

To study mass diffusivity, Fig. 11 shows mean square displacements of O atoms along the z direction, which are calculated using the simulation data for 0-3 ps. The solid and dashed lines are obtained from O atoms in the interfacial and Fe-side regions, respectively. Here, the boundary between iron-oxide and aluminum-oxide at each interface is located by calculating the average z coordinate of Al atoms facing Fe atoms. The interfacial regions are then defined as slabs with a thickness of 4 Å (i.e. 2 Å above and below the boundaries) parallel to the \( xy \) plane as shown in Fig. 10. Figure 11 shows that O atoms in the interfacial region are much more diffusive than those on the Fe side. The four-fold accelerated diffusion constant perpendicular to the interface is \( 2 \times 10^{-4} \text{ cm}^2/\text{s} \) in the interfacial region.

To understand the mechanism of the enhanced diffusivity at the interface, we have examined the time evolution of the atomic configuration in the interfacial region and found a concerted metal-oxygen flip mechanism. That is, O atoms switch their positions with neighboring Al atoms while diffusing in the z direction. A typical example of such events is shown in Fig. 12, where the middle panel shows the time evolution of the z coordinates of the O and Al atoms of interest. The O atom moves upward in concert with the Al atom moving downward. The switching motion between the O and Al atoms is shown in the bottom panel of Fig. 12.

To explain the quantum-mechanical origin of this mechanism, we calculate the bond-overlap population \( O_{ij}(t) \) between \( i \)th and \( j \)th oxygen atoms as a function of time \( t \). We also define the sum of the bond-overlap population (SBOP) for each oxygen atom: Partial SBOP \( O_{ij}^\alpha(t) \) for the \( i \)th oxygen atom is defined as

\[
O_{ij}^\alpha(t) = \sum_{j \in \alpha} O_{ij}(t),
\]

where \( \alpha \) is Fe or Al; and the total SBOP is \( O_i(t) = O_{i\text{Fe}}(t) + O_{i\text{Al}}(t) \). The upper panel of Fig. 25 shows \( O_i(t) \) and \( O_{i\text{Fe}}(t) \) associated with the O atom. For \( t < 2.3 \) ps, the oxygen atom resides in the iron-oxide region, and \( O_{i\text{Fe}}(t) \) has finite values, while \( O_{i\text{Al}}(t) \) is nearly zero. At \( t \sim 2.3 \) ps, the oxygen atom starts to migrate into the aluminum side and \( O_{i\text{Al}}(t) \) begins to increase. For \( 2.3 \) ps < \( t < 2.7 \) ps, \( O_{i\text{Fe}}(t) \) and \( O_{i\text{Al}}(t) \) have comparable values while the oxygen atom is moving across the interface. For \( t > 3.0 \) ps, \( O_{i\text{Fe}}(t) \) becomes zero, while \( O_{i\text{Al}}(t) \) converges to a finite value, indicating that the oxygen atom is chemically bonded only with Al atoms. The switching motion between O and Al atoms at the interface is thus triggered by the change of chemical bonding associated with these atoms.

To quantify the collective switching motion between O and Al atoms, we calculate the correlation function between the displacements of atoms along the z direction:

\[
d_{O-Al}(t)=\frac{\langle \Delta z_i(t) \cdot \Delta z_j(t) \rangle}{t^2},
\]

where \( \Delta z_i(t) = z_i(t+t_0) - z_i(t_0) \) with \( z_i(t) \) being the z coordinate of the \( i \)th ion at time \( t \). The brackets mean the average over both the time origin \( t_0 \) and atomic pairs \( (i \in \text{O}, j \in \text{Al}) \). In the calculation, atomic pairs whose distance is less than 2.3 Å at \( t_0 \) are selected. Since we are interested in the correlation between diffusing O and Al atoms, we include atomic pairs that satisfy the conditions \( |\Delta z_i(T)| > 2 \text{ Å} \) and \( |\Delta z_j(T)| > 2 \text{ Å} \) at \( t = 2 \) ps. The results in Fig. 13(a) (solid curve) reveal negative correlation in \( d_{O-Al}(t) \) for \( t < 0.5 \) ps, which reflects the collective switching motion between O and Al atoms at the interface as shown in Fig. 12. Such negative correlation does not exist on the Al side (see the dashed curve in Fig. 13(a)), indicating independent diffusive motions of Al and O atoms.

The enhanced mass diffusivity at the metal-oxide interface leads to a two-stage reaction behavior. In Fig. 13(b), we plot the position \( z_i(t) \) of the reaction front calculated from the coordinates of oxygen atoms at the forefront of oxidation. For \( t < 1 \) ps, \( z_i(t) \) increases rapidly as oxygen atoms migrate into the Al side, which is accelerated by the collective switching mechanism. This is followed by a slower reaction due to uncorrelated diffusion of atoms. (Though slower than the concerted thermite reaction, the second-stage diffusion here could still be faster than conventional diffusion, due to defect-mediated giant diffusivity because of the depletion of O atoms in the near-interface oxides.) Such two-stage reactions may be related to the experimental observation in thermite nanowire arrays mentioned before.

Collaborations and Technology Transfer
The atomistic understanding gained in this project will lead to the development of new and improved materials and structures with enhanced energy density and reduced sensitivity for a wide range of DoD applications, by significantly accelerating the pace of experimental research and through our extensive collaborations with DoD scientists (Dr. William Wilson at DTRA; joint paper “multimillion atom reactive simulations of nanostructured energetic materials” in Journal of Propulsion and Power with Dr. Barrie Homan and Dr. Kevin McNesby at ARL; our students’ internships with Dr. Betsy Rice and Dr. Margaret Hurley at ARL; and mutual visits by Dr. Brad...
Forch and Dr. Shashi Karna at ARL). Our dual-degree students (Ph.D. in the physical sciences or engineering with MS in Computer Science specialized in High Performance Computing and Simulations) continue to do internships with our DoD collaborators.

**Resulting Journal Publications During Reporting Period**


**Graduate Students Involved During Reporting Period**

- Richard Clark (Ph.D., current)
- Weiqiang Wang (Ph.D., graduated)

**Awards, Honors and Appointments**

![Flowchart](image)

**Fig 1:** Flowchart of runaway reaction leading to burning.
Fig. 2: (a) Temperature of particle during nanosecond simulation. (b) Rate of temperature change in system. Shift from confined burn into spallating burn (identified by red arrow).

Fig 3: Radial temperature of particle during initiation phase. Initial heating seen at core-shell (inner) boundary.
Fig 4: Fragment analysis of ANP during initiation phase.

Fig 5: Time variation of the inner radius of shell boundary, showing increasing penetration of oxygen into core area throughout phase.

Fig 6: Snapshots of central slice of particle during burn, hiding core Al atoms to allow viewing of oxygen penetration at 0 and 100 ps.
**Fig 7:** Graph of aluminum atoms present outside the outer shell boundary (i.e., ejected or spalled atoms). Shows transition from confined burn to spallation burn.

**Fig 8:** Fragment analysis of ANP during spallation burn phase, showing dramatic increase in oxygen-rich fragments.
Fig 9: Snapshots of particle at 200 and 800 ps. Core aluminum atoms have been removed to show oxidation throughout core.

Fig. 10: Snapshots of the atomic configuration. The green, red and grey spheres show the positions of Fe, O and Al atoms, respectively. Yellow meshes at time 0 ps show
the non-overlapping cores used by the DC-DFT method. Two interfacial regions are defined as slabs with a thickness of 4 Å parallel to the $xy$ plane (length scale in angstrom is marked in the $z$ direction). The Al- and Fe-side regions are defined between the two interfacial regions as shown in the figure.

![Graph](image)

**Fig. 11:** Enhanced diffusion at the metal-oxide interface. Mean square displacements of O atoms along the $z$ direction are plotted as a function of time. The solid and dashed curves are for O atoms in the interfacial and Fe-side regions, respectively.
**Fig. 12**: Concerted metal-oxygen flip mechanism. (Top panel) Time evolution of the total and partial SBOP, $O(t)$ and $O'_i(t)$, associated with the oxygen atom labeled as ‘O’ in the bottom panel. The black, red and blue curves show $O(t)$, $O_{Fe}^i(t)$ and $O_{Al}^i(t)$, respectively. (Middle panel) Time evolution of the $z$ coordinates of the O and Al atoms labeled as ‘O’ and ‘Al’ in the bottom panel, respectively. (Bottom panel) Atomic configurations near the O and Al atoms of interest (labeled as ‘O’ and ‘Al’) at 2.3 and 2.8 ps. The green, red and blue spheres are Fe, O and Al atoms, respectively.

**Fig. 13**: (a) Negative correlation associated with concerted Al and O motions at the interface. Correlation functions between displacements of O and Al atoms along the $z$ direction (defined in Eq. (1)) are shown as a function of time. The solid and dashed curves are obtained in the interfacial and Al-side regions. (b) Two-stage reactions of thermit. Time evolution of the positions $z_c(t)$ of the reaction fronts. The gray shade highlights the rapid first-stage reaction due to concerted Al-O motions, which is followed by slow reaction based on uncorrelated diffusion.
Objective

Nano-aluminum particles are used in many propulsion and energy-conversion applications due to their increased reactivity, which results from higher specific surface area and reduced activation energies for chemical reactions. Uncertainties and inconsistencies, however, still exist in the present theories describing nano-aluminum ignition and combustion phenomena. Furthermore, coating of selected metals (e.g., nickel) over aluminum particles is found to reduce the particle ignition temperature significantly. The objective of this research is two-fold: (1) to clarify several fundamental issues pertinent to nano-scale aluminum ignition and combustion; and (2) to investigate the thermodynamics of nickel-coated aluminum particles by means of molecular-dynamics simulations. The reduction in the ignition point at all length scales by nickel coating is quantified, and a phenomenological theory describing the ignition characteristics of nickel-coated aluminum particles is developed. The theoretical/numerical framework established can be used to investigate the effects of other metallic coatings on nano-aluminum particles.

Approach

The following are the important steps taken towards the fulfillment of the objective:

- At first, a comprehensive review on ignition and combustion of aluminum particles at micron and nano scales was conducted.
- Molecular dynamics studies were performed to examine the thermodynamic behavior of aluminum particles at nano scales.
- Based on the review and results of molecular dynamics studies, a multi-scale theory of ignition and combustion of aluminum particles was proposed. The theory accommodates a wide range of length and time scales, and resolves many inconsistencies found in the literature.
- A generalized numerical framework was implemented to accommodate potential functions capable of handling thermodynamics of nickel, aluminum, and nickel-aluminum interactions.
- The computer code was benchmarked against available experimental data.
- The code is currently being used to study the thermodynamic behavior of nano-aluminum and nano-nickel particles with different sizes.
Relevance to Army

A comprehensive and quantitative knowledge base is obtained of combustion and ignition of nano aluminum and nickel-coated aluminum particles. The theoretical framework and computational methodology developed can be applied to a variety of nano metal particulates. Results secured from this study will help devise novel methods and materials to improve the ignition characteristics of energetic particles. In addition, a substantial knowledge base on ignition and combustion of aluminum particles at all scales will be furnished.

Accomplishments for Reporting Period

- A comprehensive review on ignition and combustion of aluminum particles at micron and nano scales.
- Establishment of a unified theory of ignition and combustion of aluminum particles for a wide range of sizes, from nano to meso scales.
- Development of a general framework capable of handling nickel-aluminum interactions for the study of thermodynamic behavior of nickel-coated aluminum particles. The model has been benchmarked against the phase transition of bulk nickel and bulk aluminum.

Collaborations and Technology Transfer

The research results (modeling techniques and research findings) will be transferred to ARL and other DoD laboratories to help devise novel methods and materials for improving the ignition characteristics of energetic particles, and to maximize the utilization of nano metal particles for propulsion and energetics applications.

Resulting Journal Publications During Reporting Period


Graduate Students Involved During Reporting Period

- Puneesh Puri (Ph.D., Graduated in December 2008, currently at Intel, Inc.).
- Dilip Srinivas Sundaram (Ph.D., Current; M.S., Graduated in August 2009)

Awards, Honors and Appointments

- Propellants and Combustion Award, 2009
- American Institute of Aeronautics and Astronautics
Objective
The objective of this work is to understand the fundamental mechanisms of energetic materials containing nanoparticles using laser flash-heating combined with ultrafast spectroscopy. Interfacing with researchers who synthesize and engineer new nanomaterials and theorists who study mechanisms of nanoenergetic combustion will lead to bottom-up methods of designing nanoenergetic materials for DoD applications. A secondary objective added this year as a result of the add on is to develop technologies to study the high-speed impact dynamics of reactive nanomaterials.

Approach
- Ultrafast infrared spectroscopy combined with laser flash-heating is used to study molecular mechanisms of chemistry and nanoscale transport
- Ultrafast emission spectroscopy is used to study reactions of metals with oxidizers and to study the time scales of energy release
- Time-resolved nonlinear or multidimensional spectroscopies are used to understand heat transfer over short distance scales of a monolayer or nanoparticle
- Ultrafast microscopy is used to characterize the explosive behavior of nanogram or microgram quantities of prototype materials
- Laser-driven flyer plates are developed to study impact initiation of nanoenergetic materials

Relevance to Army
Nanotechnology is a promising method of making new munitions, but the processes which determine the performance of nanotechnology munitions lie in a realm in between the better-known engineering models of bulk materials and chemical reaction dynamics of molecules, and are not well understood yet. Nanotechnology also offers the possibility of an unprecedented level of control over the structure of a munition on length scales from nanometers to meters. However we do not yet have a firm understanding of the relationships between nanostructure and performance and how to design optimal devices for specified tasks. A particularly important application is reactive materials for low collateral damage bomb casings. In order to improve the design of materials for such applications, we need a fundamental understanding of how reactive nanomaterials are initiated and how they fragment upon high speed impact.

Accomplishments for Reporting Period
• Using our improved flash-heating emission spectroscopy apparatus, we have studied laser ignition of a variety of nanoparticle composites, consisting of 50 nm Al particles, either in a neat thin film, or with oxidizers nitrocellulose and teflon and with inert polybutadiene. These materials have been studied as a function of laser ignition pulse energy and particle concentration.
• The thermal response of self-assembled monolayers on metal surfaces has been studied using a flash-heating technique combined with ultrafast nonlinear coherent vibrational spectroscopy.
• A laser-driven flyer plate apparatus has been developed. It consists of a launch laser with a state of the art beam shaper to produce top hat beams, a microfabricated laser flyer plate array, and a variety of high speed diagnostics to monitor flyer plate launch including a fast imaging system and an 8 GHz displacement interferometer. Flyer plates 0.8 mm in diameter have been launched having velocities up to 4 km/s.

Collaborations and Technology Transfer
• Research discussed extensively with collaborators at DOE labs LANL, LLNL and Argonne
• Discussed simulations of self-assembled monolayers with Vashishta at USC
• Discussed spectroscopy of fluorocarbon-coated nanoparticles with Jason Jouet of NSWC

Resulting Journal Publications During Reporting Period

Papers presented at meetings
1. (invited) Columbia University Department of Chemistry, Oct. 2008, "Vibrational energy with high time and space resolution".
2. (invited) Army Research Office Review of Insensitive Munitions Multiuniversity Research Initiative, University of Missouri, Jan. 2009, "Spectroscopic observation of structures and molecular response at surfaces of energetic materials"
5. (invited) International Conference on Time Resolved Vibrational Spectroscopy (TRVS), New Hampshire, May 2009, "Vibrational dynamics at interfaces probed by vibrational sum-frequency generation spectroscopy"
6. (invited) ACS Colloids and Surface Chemistry Symposium, Columbia University, June 2009, "Vibrational dynamics at interfaces probed by vibrational sum-frequency generation spectroscopy".
8. Telluride workshop on Vibrational Dynamics, Telluride, CO, July 2009, "Vibrational energy transport in molecules".
9. Pinhead Institute Town Talk, Telluride Conference Center, Telluride, CO, July 2009, "The science of explosions: Blowing things up for fun, profit, war and medicine".

Graduate Students Involved During Reporting Period

Awards, Honors and Appointments
- Jeffrey A. Carter: Merck Fellowship in Analytical or Physical Chemistry
- Dana D. Dlott: Lycan Professor of Chemistry
Concept for laser-driven miniflyer studies of reactive material (RM) dynamics. top. A miniflyer impacts the RM against a transparent witness plate at velocities of 0.1 - 5 km/s. A 25 ps streak camera spectrograph detects the emission burst. A displacement interferometer (DISAR) monitors the flyer velocity history. bottom: The RM impacts a screen causing it to fragment. The fragments are monitored using ultrafast microscopy. The DISAR measures the time dependent velocity distribution.

Laser and beam shaping system. Raw output laser beam profile is shown at bottom. z1 and z2 are zoom lens assemblies. Images: (a) raw output. (b) After 30 m propagation. (c) After beam shaper. (d) Top hat beam 0.8 mm in diameter in the plane of the shock target array.
Block diagram of fiberoptic displacement interferometer for any reflector DISAR.

Oscilloscope traces showing the launch laser pulse and the emission from flyer plate impact with window. Right. Velocity measurement plotting $\Delta t$ versus distance in 25 $\mu$m steps for a 2 $\mu$m thick Al flyer plate.

Photo of Hiroki Fujiwara and Kathryn E. Brown with flyer plate apparatus.
Objective

The goal of this MURI effort is to study the reactivity and combustion characteristics of nano engineered energetic materials (NEEMs). As part of this program, we are also studying the fabrication of nano-engineered energetic materials via self assembly of nano particulate ingredients into organized structures at the microscale. This past year, efforts concentrated on electrostatic self-assembly of nanothermite microspheres. The research seeks a fundamental understanding of the relationship between the structures of nano-engineered energetic materials and their reactive and mechanical behavior, particularly with regard to sensitivity, ignition, burning characteristics, and optimum loading density, thus enabling design optimization of NEEMs.

Approach

- Constant pressure and constant volume combustion experiments are used to determine reaction rates, propagation speeds, and chemical efficiency of nanoengineered energetic materials (NEEMs).
- High speed photography, emission and infrared spectroscopy, and gas chromatography are used to develop detailed understanding of the physical and chemical mechanisms of reacting NEEMs.
- Thermogravimetric analysis and differential scanning calorimetry are used to study the thermal behavior of NEEMs.
- Electrostatic self-assembly is utilized to create self-assembled nanothermite microspheres (SANTMs) from a bottom-up approach.

Relevance to Army

Historically, it is well known, although not well understood, that a strong correlation exists between the energy density of an energetic material and its sensitivity. The successful development of NEEMs may provide the means to unravel and control this relationship. The program
outcome will help enable DoD to fabricate molecularly designed energetic materials at the nano-scale with tuned chemical and physical properties that yield improved performance and reduced sensitivity, and the possibility of multi-functionality.

**Accomplishments for Reporting Period**

- Experiments to better understand the propagation mechanisms of nanothermites have been continued this period. The reaction temperature, the heating rate, and the reaction zone thickness are critical parameters to understanding these mechanisms. Measurements of the reaction temperature for the Al/CuO system were made using a multi-wavelength pyrometry for two different configurations. In one experiment, the radiative emissions were collected from a single spot on an instrumented burn tube filled with the nano-thermite as the combustion wave passes and temporal change of temperature was measured. In the other experiment, the radiative emissions were collected from a small, unconfined pile (~10mg) of the Al/CuO nanothermite was collected over a 50 ms integration time and the average temperature was measured. The average time integrated temperature from the unconfined pile experiment was 2390±150 K. The average plateau temperature for the temporally resolved measurements was approximately 2250±100 K, while the constant pressure, adiabatic equilibrium temperature is 2770 K. The reaction zone thickness was approximated to be on the order of 40mm, which is much larger than a typical gas-phase hydrocarbon-air flame for which laminar flame theory is based on. The important conclusion from the temperature measurements is that the reaction temperature is below the vaporization temperature of Cu and Al. Consequently, the gas that is formed from the reaction is likely from the decomposition of CuO, which happens at temperatures close to 1400 K at 1 atm, where a phase change from CuO to Cu_2O releases oxygen gas. The gas that forms, mainly molecular oxygen, then reacts with the aluminum heterogeneously to form alumina. Hence the pressure disturbance that propagates the reaction is a result of intermediates that are formed and not products.

- Experiments were conducted on the reaction propagation of Al/CuO and Al/MoO_3 thermites in which the sizes of the fuel and oxidizer particles were varied between the nanometer and micron scale. Critical properties, including combustion velocities, dynamic pressure, and spectral emission, were measured and compared to determine if the scale of one constituent has more influence over the rate of propagation than the other. To measure combustion velocities and dynamic pressures, experiments were performed where the thermite mixtures were loosely packed in an instrumented burn tube and ignited by a heated nichrome wire. It was found that, although nano-fuel/nano-oxidizer composites were the fastest for both the Al-CuO and Al-MoO_3 thermites, composites containing micron-Al and a nano-scale oxidizer propagated much faster than a composite of nano-Al and a micron-scale oxidizer. Since particles at micrometer scale have a much higher packing density than nanoparticles, it was desirable to know the effects of density in a semi-confined burning configuration. Experiments showed the effect of density on propagation rate was not significant for small changes, however problems with the mixtures igniting during compaction hindered the study of densities greater than 20% TMD, preventing the testing of nano-scale thermites at the same densities as their micron-scale counterparts.

- The effect of stoichiometry on the combustion behavior of the nanoscale aluminum molybdenum trioxide (nAl/MoO_3) thermite was studied in collaboration with Steve Son in a burn tube experiment by characterizing the propagation velocity and pressure output of the reaction. Changing the stoichiometry affects the combustion through changes in the product temperature, phase, and composition. The mixture ratios of the composites were varied over an extremely wide range (5% nAl (95% MoO_3)–90% nAl (10% MoO_3)). Results revealed three separate combustion regimes: a steady high speed propagation (~100-1000 m/s) from approximately 10% to 65% nAl, an oscillating and
accelerating wave near 70% nAl, and a steady-slow speed propagation (~0.1–1 m/s) from approximately 75% to 85% nAl. Propagation was observed to fail both <10% nAl and >85% nAl. The instrumented tube tests revealed peak pressures over 8 MPa near stoichiometric conditions in the steady high speed propagation region, no measurable pressure rise at low speed propagation, and building pressures for accelerating waves. The results suggest the propagation mode to be a supersonic convective wave for near stoichiometric mixtures and a conductive deflagration for extremely fuel-rich mixtures.

- Nano-scaled aluminum and nickel powders have been mixed into reactive composites. These composites have then been placed into tubes and ignited while being recorded with a high speed camera. The resulting videos were analyzed to determine propagation rates. The percentage of Al was varied during the tests to determine the effects of variation of stoichiometry. Results indicate that Al lean and rich mixtures burn slightly faster than the stoichiometric mixture. All propagation rates were on the order of 1 cm/s. The effects of powder density on propagation rate have been studied. Although it was anticipated that by decreasing the distance between the particles, diffusion and conductive heat transfer would be enhanced through the composites, initial results show a slight decrease in propagation velocity with increasing density.

- In collaboration with Dave Allara and Orlando, research is currently underway to identify parameters important to the reaction of metal foils composed of many alternating layers of aluminum and nickel with thicknesses on the order of tens of nanometers. The new contribution of this work is to investigate the effects of self assembled mono-layers (SAMs) between some of the foil layers on the reactive and mechanical properties of the foils. During this period, multilayer foils were fabricated via sputter coating and the current challenges include identifying SAMs that can withstand the conditions present within the sputter coating chamber and separating the foils from their silicon wafer substrate.

- With Tim Eden, efforts are currently underway in collaboration with John Potter at the Applied Research Laboratory at Penn State and Matthew Trexler at the Army Research Laboratory to produce highly dense bulk reactive materials consisting of Al and other metals such as Ni and Ti using the cold spray process. This process involves injecting micron scale powders into a high speed gas jet. The powder-seeded gas flows through a nozzle that greatly increases its speed. When the jet impacts a substrate the entrapped powder deforms and a material layer is built up with a density that approaches that of the bulk powder constituents. The thermodynamics of several reactive mixtures have been studied and the cold spray process has already been used to generate various bulk materials, some of them reactive. These studied complement the foil studies where the effect of varying the surface chemistry of the initial powders by adding SAMs and other materials to the mixture to modify its mechanical and chemical properties is being investigated.

- The heterogeneous interaction between nitromethane (NM) and particles of nanoscale aluminum (38 and 80 nm diameter) and fumed silica are examined in terms of both deflagration and detonation characteristics. Burning rates are quantified as functions of overall mixture burning rate using an optical pressure vessel up to 14.2 MPa, while detonation structure is characterized in terms of failure diameter. Nitromethane is gelled using fumed silica (CAB-O-SIL), as well as by the nanoaluminum (nAl) particles themselves. Use of the nanoaluminum particles slightly increases burning rates compared to larger diameter particles, however distinct increases in burning rates are found when CAB-O-SIL is removed and replaced with more energetic aluminum nanoparticles, whose high surface area allow them to act as the gellant. Mixtures including fumed silica show reduced burning rate pressure exponents compared to neat NM, while mixtures of aluminum particles alone show a significant increase. Failure diameters of mixture detonations are found to vary significantly as a function of 38 nm aluminum particle loading, reducing more than 50% from that of neat nitromethane with 12.5% aluminum loading. Failure
diameter results indicate a relative minimum with respect to particle separation (% loading) which is not observed in other heterogeneous mixtures.

Collaborations and Technology Transfer

- Collaboration with Prof. Ralph Nuzzo and Prof. Greg Girolami of UIUC on the combustion of nano boron systems.
- Collaboration with Prof. Dave Allara and Orlando of Penn State on the reactivity and combustion of Al-SAM-CuO and Al-SAM-Ni thin films.
- Collaboration with Prof. Steve Son of Purdue on the combustion of nanothermites and nano aluminum-liquid oxidizer mixtures.
- Collaboration with Matthew Trexler at the Army Research Laboratory on cold spray of reactive materials and combustion analysis.
- Collaboration with Tim Foley and Blaine Asay at LANL on gelled explosives self-assembly of nanothermites.

Resulting Journal Publications During Reporting Period

Graduate Students Involved During Reporting Period
  • Justin Sabourin (Ph.D., current)
  • Mike Weismiller (Ph.D., current)
  • Steven Dean (Ph.D., current)

Undergraduates Involved During Reporting Period
  • Bruce Yang (Senior, current)

Awards, Honors and Appointments
Left: Example of emission data taken by streak camera experiment. The vertical axis is time and the horizontal axis is wavelength. Right: Intensity and temperature versus time results for Al/CuO (Φ=1.1) nanothermite burn tube experiment.