R1-A.2: Characterization of Energetic Materials Under Extreme Conditions

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II. PROJECT DESCRIPTION

A. Project Overview

We have determined static properties for a selected set of energetic materials of common interest to the projects in the R1 thrust, especially nonconventional energetic materials such as triacetone triperoxide (TATP)—the explosive used in the recent terror attacks in Paris (2015) and Brussels (2016)—in collaboration with the R1-C2 project at the University of Rhode Island (URI). The URI research group has provided the sample material, while the Washington State University (WSU) project has examined the phase and chemical stability of TATP under high pressures using micro-Raman spectroscopy and synchrotron X-ray diffraction. The results show that TATP undergoes pressure-induced structural changes, initially to a new crystalline phase at 7 GPa and then to amorphous solid above 30 GPa.

We have also made significant progress on the development of time-resolved spectroscopic (TRS)/X-ray diffraction (TRX) capabilities for dynamic properties of reactive materials—a class of newly emerging nonconventional explosives. The TRX experiments were performed on several reactive metal composites including nickel (Ni) and aluminum (Al) composites with boron, nitrogen, ammonium nitrates (AN), and ammonium perchlorate (AP) using the nation’s brightest hard X-ray source at the Advanced Photon Source (APS). We obtained quantitative information on the chemical and structural evolution of reactive materials undergoing metal combustions, intermetallic reactions, and thermit reaction. The first set of TRX experiments have been completed. The results on Ni and Al composites with boron and nitrogen were quite successful. However, the results for metal dispersed AN and AP were not successful because their ignition (well below 1 μs) is substantially faster than our time-resolution of TRXdiffraction (~30 μs). Thus, we are planning to investigate the ignition characteristics of metal dispersed AN and AP using nanoseconds (ns) time-resolved temperature measurements in the coming year.

This project has provided the opportunity for two graduate students to gain hands-on experience with cutting-edge technologies and technical issues associated with fundamental research on energetic materials related to Department of Homeland Security (DHS) and Department of Defense (DoD) programs. We have also produced four major technical manuscripts in Year 3 and Year 4 (see Section IV.B for the two that relate to this reporting period).
B. Year Two (July 2014 through June 2015) Biennial Review Results and Related Actions to Address

The Biennial Review identified that this project addresses an important knowledge gap related to understanding the nature of explosives properties and what occurs during detonation. It also indicated that we provide fundamental data for various predictive codes such as the CHEETAH thermochemical code, which aids weapons designers and responders in the reactivity and stability of materials of interest. The Biennial Review recognized the significance of the methodology, including micro-Raman spectroscopy and X-ray synchrotron spectroscopy, employed in our ongoing work towards understanding the effects and properties of explosives. The review also pointed out that one of the potential weaknesses of the project is a lack of effective coordination with the R1-A.1, R1-B.2, and R1-D.1 projects, and suggested that we develop transition efforts with Los Alamos National Laboratory (LANL) and Lawrence Livermore National Laboratory (LLNL).

In response to the Biennial Review comments, we have already transmitted our Equations of State (EOS) data on I$_2$O$_5$ to theory groups at LLNL (Dr. Larry Fried) for their incorporation into the CHEETAH code. We are also collaborating with the LANL group (Dr. Dattelbaum) for TRX diffraction on carbon products using a Linear Coherent Light Source (LCLS) at Stanford University. Work is also taking place with the LLNL group (Dr. Evans) for TRX diffraction on reactive materials in dynamic Diamond Anvil Cells (dynamic-DAC). We will continue these collaborations with the LLNL and LANL groups in Year 5.

The synergy between the R1-A.1, R1-A.2, R1-B.2 and R1-D.1 projects is indeed important, as the review pointed out. Thus, we are working with the R1 project investigators to identify a homemade explosive (HME) material of common interest, and to characterize the material’s properties at high pressures and temperatures. For example, experiments on TATP have been performed in collaboration with the URI group led by Professor Jimmie Oxley.

C. State of the Art and Technical Approach

Static high-pressure properties such as melting, phase transitions, and crystal structures are important for gaining insight into chemical stabilities and reaction mechanisms of energetic materials, in general. Melting, for example, most strongly affects the chemical sensitivity and decomposition kinetics of energetic materials, ranging from simple burn to deflagration and detonation. Unusual melt anomalies are often observed, yet theoretical predictions of melt curves are difficult to make even for simple inert solids. Thus, the melt curves of energetic materials provide the most critical constraints for developing and validating reliable thermochemical models describing energetic reactions. High-pressure polymorphism and phase transitions, on the other hand, have wide-ranging consequences on the basic properties of energetic materials, such as intermolecular interaction, chemical bonding, crystal structure, thermoelastic properties, and chemical sensitivity. Two different polymorphs of the same energetic material often display substantially different properties and energetic behaviors in shock sensitivity and detonation chemistry. Importantly, the phase transition in energetic materials often triggers the chemical reaction leading to deflagration and detonation and, thus, is related to shock (or chemical) sensitivity in fundamental ways. The phase diagram provides concise and rudimentary information to understand the static and dynamic responses of energetic solids, and to develop chemical methods to mitigate the associated threats. Therefore, our approach is to investigate the phase and chemical stabilities of selected energetic materials at high pressures as well as to help characterize critical aspects of the energetic processes and, lastly, to develop novel chemical mitigation methods. This year, we have made significant accomplishments regarding two types of energetic materials in TATP and reactive materials described in the below sub-sections C.1 and C.2, respectively.

C.1. Pressure-Induced Structural Changes of TATP

High-pressure polymorphism and phase transitions have wide-ranging consequences on the basic properties of molecular solids such as intermolecular interactions, chemical bonding, crystal structures, and thermoelastic properties. One class of materials upon which this has a considerable effect is that of energetic...
materials [1,2]. Two different polymorphs of the same energetic material, for example, often display significantly different properties and energetic performance attributes such as crystal density, detonation velocity, shock sensitivity, and detonation chemistry [3,4]. Phase transitions do occur over a large pressure-temperature range in relation to chemical detonation (to 50 GPa and 4000 K) [5-7], which can alter energetic processes in a fundamental way.

There have been extensive efforts exerted towards understanding and characterizing high-pressure properties of energetic materials, including shock Hugoniot and detonation velocities under dynamic conditions in terms of continuum measurements [6, 8]. However, in comparison, there have been relatively few studies investigating pressure-induced changes at the molecular level under static high pressures [2,9]. This constitutes a major knowledge gap, especially considering that nearly all molecular solids, including most energetic materials, exhibit a profound polymorphism under high pressures as they undergo major modifications in intermolecular interaction. This typically starts at the relatively low pressures of 1-10 GPa. In this regard, high-pressure structural studies are an excellent tool for understanding and modeling not only the performance characteristics of energetic materials, but also the exact nature of chemical bonding and pressure-induced changes that lead to chemical reactions like detonation.

TATP is an organic peroxide and a primary high explosive produced by the oxidation of acetone as a mixture of linear monomeric, cyclic dimer, trimer, and tetramer forms of acetone peroxide [10]. It forms a white crystalline powder with a distinctive bleach-like order, and can explode if subjected to heat, friction, or shock. In contrast to other explosive materials driven by an excessive heat of formation, the explosion of TATP does not have thermo-chemically favored products but is predicted to be driven entropically [11]. As a non-nitrogenous explosive, TATP has historically been more difficult to detect. It has also been implicated as the explosive used in recent terrorist attacks in Europe including the 2016 Brussels bombings. Yet, little is known about its properties, especially at high pressures and temperatures. To address this, we have investigated the physical and chemical stability of TATP at high pressures, in collaboration with the URI projects.

TATP was synthesized by the URI group for the current high-pressure experiments using DAC coupled with micro-Raman and synchrotron X-ray diffraction experiments. The main findings are that TATP undergoes structural phase transitions at ~7 GPa and potentially at ~20 GPa, and eventually amorphizes above 30 GPa. There have been six different polymorphs of TATP reported at ambient pressures [12]. Of those, the present X-ray data is best explained in terms of monoclinic structure (space group P21/c) with the lattice parameters of a = 13.975 Å, b = 10.818 Å, c = 7.969 Å, β = 91.72°, and V = 1204.2 Å³, as illustrated in Figure 1 (on the next page). It is interesting that the cell volume is slightly larger (by about 3.8%) than that at ambient pressure, a = 13.788 Å, b = 10.664 Å, c = 7.894 Å, β = 91.77°, and V = 1160.1 Å³ [12]. It is not known if this volume difference is related to the large entropic origin of TATP [11]. Further studies are required to understand the chemical stability of TATP and the crystal and chemical structures at higher pressures.
Dynamic responses of reactive metals, metal alloys, and metal composites are not well understood. More specifically, we do not know how they deform, fracture, and combust; how they evolve structurally and chemically to metal oxides and intermetallic products; and how they release chemical energy under thermal and mechanical loadings. It is an integrated, multidisciplinary subject in materials chemistry and solid mechanics. These reactive materials (RMs) have been studied in large-scale integrated experiments and multi-scale hydrodynamic simulations (a top-down approach). There remains a need for small-scale, real-time experiments that can provide timely and interactive information with which to tailor materials characteristics (composition, microstructure, and bonding) for better mechanical and chemical properties as well as development of novel materials, in addition to fundamental materials data to explain large-scale, integrated experimental results and validate the individual materials models used in hydro-simulations (a bottom-up approach).

Rapid, self-sustaining thermochemical reactions of RMs are often described using simple chemical models, but their accuracies and validities are difficult to evaluate because of the complexity and transient nature of the combustion-like process. Even a “simple” process like zirconium (Zr) combustion, for example, is not simple at all, but involves rather complex structural and chemical changes: $\alpha$-Zr $\rightarrow$ $\beta$-Zr $\rightarrow$ liquid-Zr $\rightarrow$ liquid-ZrO$_2$ $\rightarrow$ $\gamma$-ZrO$_2$ $\rightarrow$ $\beta$-ZrO$_2$ $\rightarrow$ $\alpha$-ZrO$_2$, valid only for small particles [13]. In contrast, the combustion of larger particles often results in oxygen-deficient metal sub-oxides such as Zr$_2$O and ZrO and their mixtures in different phases [14]. Many of these processes occur exothermically, fueling other reactions and altering the dynamics of RMs. These processes are clearly not the same as $\text{Zr} + \text{O}_2 \rightarrow \text{ZrO}_2$, which has been assumed in commonly-used integrated chemical models and hydro-codes. Therefore, obtaining the atomistic information regarding the structural and chemical evolutions during rapidly progressing thermochemical reactions is a priority for going beyond an energetic use of reactive materials; it can be used for developing a predictive capability.

C.2. Time-Resolved Structural Changes of Al Dispersed BN Composites

Dynamic responses of reactive metals, metal alloys, and metal composites are not well understood. More specifically, we do not know how they deform, fracture, and combust; how they evolve structurally and chemically to metal oxides and intermetallic products; and how they release chemical energy under thermal and mechanical loadings. It is an integrated, multidisciplinary subject in materials chemistry and solid mechanics. These reactive materials (RMs) have been studied in large-scale integrated experiments and multi-scale hydrodynamic simulations (a top-down approach). There remains a need for small-scale, real-time experiments that can provide timely and interactive information with which to tailor materials characteristics (composition, microstructure, and bonding) for better mechanical and chemical properties as well as development of novel materials, in addition to fundamental materials data to explain large-scale, integrated experimental results and validate the individual materials models used in hydro-simulations (a bottom-up approach).

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and, ultimately, controlling the mechanical and chemical properties and bonding for better performance and energetic characteristics.

To determine real-time structure information of rapidly reacting RMs, we used the time- and angle-resolved X-ray diffraction (TARXD) configuration, analogous to one used previously [15], employing monochromatic synchrotron X-rays and a two-dimensional (2D) pixel array X-ray detector (DECRTIS PILATUS 1M-F, 981 x 1043 pixels) in combination with a fast-rotating diffraction beam chopper. This setup provides a time- (in an azimuthal direction) and angle- (in a radial direction) resolved X-ray diffraction image continuously recorded at 50 to 100 Hz with the time resolution of ~110 to 55 μs over a long period of interest (often to several hundred milliseconds (ms)).

Several types of reactive materials were investigated to elucidate chemical mechanisms for: (1) Intermetallic exchange reactions in Al2Ni to Al3Ni2 and Al3Ni, upon rapid quenching of molten phases of Al/Ni alloys; (2) Diffusion-controlled, solid-state combustion reactions in intermetallic composites of (Al2Ni + h-BN) and metallic composites (Al + h-BN) to produce h-AlN; and (3) Combustion reactions of metallic mixtures (Al + B) with N2 gas to produce metastable c-AlN. While we are preparing a publication to report the details of these results, here we show an example of a combustion-like chemical reaction in cold sintered Al + h-BN composite to h-AlN and AlB2 which occurs in solid states (see Fig. 2a). Based on the measured temperature (see Fig. 2b), it is clear that AlN is formed at ~500-700 K (at 3.3 ms after heating), well below the melting temperature of Al at 933 K. Then, the temperature reaches the highest temperature, ~2,500 K at 13.7 ms. At 20 ms after heating, AlB2 appeared and the peak shape became clear and sharp for further cooling. The heat produced from this solid-state exchange (or metathesis) reaction melts h-AlN and then quenches to the mixture of h-AlN and AlB2. The net reaction is, therefore, 3 Al + 2 h-BN = 2 h-AlN + AlB2, releasing the heat of ΔH = -194 kJ/mol. The chemical energy then heats the sample to ~2,500K, almost the same temperature where h-BN melts. The diffraction pattern at melting shows a weak signature of h-AlN buried in the molten solution of Al and BN. The reaction produces h-AlN in a hexagonal structure with the calculated lattice parameters, a=b=3.114Å and c=4.977Å, in good agreement with the previous report [16].

Figure 2: (a) A series of angle-resolved X-ray diffraction patterns of electrically ignited Al + h-BN composites, showing the formation of h-AlN; and (b) the corresponding time-resolved temperatures (black circles) recorded at 1 kHz with time-resolution of 0.1 ms (green lines), plotted together with the PILATUS frames (red lines) and the electric voltage (black lines). Note that h-AlN is formed well below Al melt temperature (933 K marked by dashed line), suggesting the solid state exchange reaction between solid Al and h-BN.
D. Major Contributions

The fundamental research outlined here will also result in scientific discoveries and technological innovations of great value to defense research needs while enabling DHS to respond to both short- and long-term national needs in the areas of explosive characterization and evaluation. Major contributions of this project to the overall ALERT research program are as follows:

Year 1:
- Completion of the investigation of chemical sensitivity of AN mixtures at high pressures and temperatures, including ammonium nitrate/fuel oil (ANFO) and Ammonal.
- Work in progress on the systematic studies of main group I peroxides, in comparison with $\text{H}_2\text{O}_2$.

Year 2:
- Completed the phase diagram of AP over the extended region of pressures and temperatures.
- Accomplished the systematic understanding of high-pressure-temperature behaviors of the main group I peroxides.

Year 3:
- Completed the investigation of AP and $\text{Li}_2\text{O}_2$ under static conditions over a wide range of pressure-temperature regimes.
- Developed a fast, time-resolved, six-channel pyrometer for the investigation of reactive metals and composites undergoing energetic metal combustions and thermite and metathesis reactions.

Year 4:
- Completed the investigation of TATP under static conditions to 60 GPa using Raman and synchrotron X-ray diffraction.
- Determined the structural evolution of reactive composites (Al dispersed BN) using the TRX experiments.

E. Milestones

In Year 4, we have completed the investigation of TATP at high pressures and ambient temperatures, which will be continued at high pressures and high temperatures. We have also completed the first set of TRX experiments in Year 4. The results on Ni and Al composites with boron and nitrogen were quite successful, but the results of metal dispersed AN and AP was not because of its substantially faster ignition (well below 1 $\mu$s) than our time-resolution of TRX diffraction ($\sim$30 $\mu$s). Therefore, we are planning to investigate the ignition characteristics of metal dispersed AN and AP using ns time-resolved temperature measurements in Year 5. In Year 5, we will also determine the dynamic responses of energetic materials, including nitromethane and TATP, in dynamic-DAC, capable of precisely controlling pressure and compression rates that can bridge the gap between conventional DAC and shock wave experiments.

F. Future Plans

In Year 5, we plan to:
- Investigate the physical and chemical stability of TATP at high pressures and high temperatures.
- Determine the dynamic responses of energetic materials, including nitromethane and TATP, in dynamic-DAC.
- Investigate the ignition characteristics of metal dispersed AN and AP using ns time-resolved temperature measurements.
- Transmit the fundamental materials data to various energetic materials libraries, including the CHEETAH
code, where the fundamental thermochemical data are limited for nonconventional energetic materials and metal thermites reactions.

- Publish the main findings in peer-reviewed journals.

We expect to accomplish these milestones within the remainder of Year 4 and Year 5, as well as achieve the final goal of measuring fundamental thermoelastic properties under both static and dynamic conditions. The fast (ns) time-resolved spectro-pyrometer developed in this project is very powerful and should be capable of measuring ns-time-resolved temperatures of explosives in detonation, thereby evaluating the detonability and dynamics of explosives. If this project receives Year 6 funding, we plan to transition this technique to measuring fast time-resolved temperatures of detonating explosives. Note that the temperature of shocked materials and/or detonating explosives are typically calculated, not experimentally measured, which remains as the largest uncertainty despite its significance in understanding the dynamics, performance, and reliability of shocked explosives. Furthermore, we are currently acquiring the X-ray Free Electron Laser (XFEL) beam-time at the Stanford Linear Accelerator Laboratory (SLAC) for femto-second (fs) time-resolved X-ray diffraction on laser-shocked materials, which will complement the present μs time-resolved X-ray studies on reactive materials, as well as the Year 6 proposed ns time-resolved temperature measurements on detonating explosives. Therefore, part of our plan for Year 6 is to examine the feasibility of probing a “very” early stage (less than the first 1 ns) of explosive detonation using the XFEL. The success will certainly lead us to a new project that can be the next step of the present DHS project.

III. RELEVANCE AND TRANSITION

The present project provides significant understanding of the fundamental properties of energetic materials of high value to DHS interests: melting, phase transition, chemical stabilities, EOS, etc. This data is critical to development in:

- Predictive capabilities for explosive initiation.
- Improved EOS models for better assessment of blast effects.
- Blast-/shock-mitigating materials and methodologies.
- Related basic science needs for materials in extreme conditions.

A. Relevance of Research to the DHS Enterprise

Our project addresses the scientific and technological challenges to detect, evaluate, and mitigate the blast effects of nonconventional energetic materials by providing: (1) Fundamental data for energetic materials libraries and thermochemical models over a wide range of phase space – critical to developing a predictive capability; (2) High-pressure data of energetic materials in relation to shock sensitivities and detonabilities for other efforts within ALERT, as well as other defense programs in DoD and the Department of Energy (DOE); and (3) Timely and “small-scale (<1μg)” evaluation of detonability and sensitivity of newly developed and/or emerging energetic materials, prior to more elaborate shock-wave experiments, without incurring safety concerns associated with large-scale synthesis.

B. Potential for Transition

Products of this project with the potential for transition to fundamental research include:

- Fundamental data to chemical data libraries to improve/validate thermochemical models, such as CHEETAH and Reactive Models developed by our collaborators (Drs. Fried and Tarver) at LLNL. These codes are used in integrated hydro-codes such as AL3D and SHAMRC used by DHS.
• Laser spectroscopic and X-ray diffraction methodologies to detect and characterize reactive materials in extreme conditions.
• Forensic (<1 μg) evaluation of energetic materials under dynamic conditions.
• Technology transfer to fundamental studies of explosives; for example, the fast (ns) time-resolved spectro-pyrometer developed in this project is powerful enough to investigate the detonation dynamics of explosives. Therefore, if this project should receive Year 6 funding, we will first transition this technique to measuring fast time-resolved temperatures of detonating explosives. Then, we will examine the feasibility of probing a very early dynamic of detonating explosives utilizing the XFEL at the SLAC. The success will no doubt lead to a new project that can be an exit strategy of the present DHS project.

C. Data and/or IP Acquisition Strategy

Fundamental data describing: (1) Thermal and chemical stabilities, and (2) Chemical kinetics and energetics of high impact explosives, will be produced in the project and then used to develop and/or validate the relevance chemical models used in CHEETHA and reactive materials hydro-codes. The materials data and information obtained in this project will also be published in scientific journals to evaluate the significance and accuracy of results via the peer-reviewed processes and for a greater level of distribution.

D. Transition Pathway

The major transition pathway of the present research is through scientific publications, student training for the future homeland security and defense workforce, data incorporation into the energetic materials data library, and the database of various thermo-mechanical and chemical codes.

E. Customer Connections

The relevant technologies, such as fast TRX diffraction and dynamic-DAC, are of great interest to the scientists at DOE and DoD laboratories, including our collaborators at LANL (Dr. Dattelbaum) and LLNL (Drs. Evans and Zaug).

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Provided research experience for undergraduate student, Austin Biaggen (Junior, Physics, WSU).
2. Provided technical training for one post-doctoral scientist on fundamental research programs related to DHS and DoD needs.

B. Peer Reviewed Journal Articles


Pending

V. REFERENCES


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