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

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II. PROJECT DESCRIPTION

A. Project Overview

Understanding the dynamic response of solids under extreme conditions of pressure, temperature, and strain rate is a fundamental scientific quest and a basic research need in materials science. Specifically, obtaining an atomistic description of structural and chemical changes of solids under rapid heating and/or compression over a large temporal, spatial, and energy range is challenging but critical to understanding material stability or metastable structure, chemical mechanism, transition dynamics, and mechanical deformation of energetic materials. In this front, we have developed time-resolved spectroscopic (TRS)/X-ray diffraction (TRX) capabilities for the investigation of dynamic properties of reactive materials—a class of newly emerging nonconventional explosives, using the nation's brightest hard X-ray source at the Advanced Photon Source (APS). We have recently applied these technologies and obtained quantitative information on the chemical and structural evolution of reactive metals and metal alloys that undergo metal combustions, intermetallic reactions, and thermite reactions. However, the progress on metal-dispersed explosives has been limited due to the challenges in preparing consistent composite samples and probing faster dynamic process occurring in these materials in ms. In Year 5, to overcome these challenges, we have developed a systematic synthesis method of high-quality metal-dispersed reactive composite, Al dispersed in Teflon, AN and AP, and a fast time-resolved optical pyrometric method to measure the temperature evolution of short-pulse laser-blasted Al-Teflon composites, as described in Section B.1.

The presence of shear in explosives plays a critical role to control shock initiation and sensitivity of energetic materials. To understand the role of shear in explosive detonation, we have investigated high-pressure behaviors of pentaerythritol tetranitrate (PETN) under quasi-hydrostatic and non-hydrostatic conditions. PETN, one of the most powerful explosives in use today, is known to exhibit highly anisotropic shock sensitivity. Indeed, our results show that PETN undergoes shear-induced chemical decomposition in nonhydrostatic condition, whereas is chemical inert in hydrostatic conditions, as described in Section B.2. In order to understand the chemical mechanisms associated with the observed decomposition, we are currently investigating

PETN in dynamic-diamond anvil cell (d-DAC), which is capable of precise controls of pressure, compression rates and shear strains.

Understanding the phase and chemical stabilities of energetic materials at blast-relevant pressure, temperature conditions has been a central theme to the present project. Continuing this emphasis, we have investigated high-pressure stability of triaceton triperoxide (TATP) —the explosive used in the recent terror attacks in Paris (2015) and Brussels (2016)—in collaboration with Project R1-C2 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 have shown that TATP undergoes pressure-induced structural changes, initially to a new crystalline phase at 7 GPa and then to amorphous solid above 30 GPa. To gain physical/chemical insights into the observed phase transitions, the additional experiments are planned.

This project provided the opportunity for three graduate and one undergraduate 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. This project also produced one new PhD (Dr. Sakun Duwal) in May 2018 in Chemistry, WSU, who will join the Los Alamos National Laboratory this summer.

B. State of the Art and Technical Approach

B.1. Aluminum Dispersed Teflon: Preparation of Composites and Short Pulse Laser Ignition

The dynamic response of reactive composite such as metal-dispersed explosives is complex and undergoes very complex energetic processes ranging from simple decomposition to deflagration and detonation [1]. The characteristics of these processes strongly depend on the extrinsic properties of reactive composites such as the density, microstructure, particle sizes, and defects. Therefore, to obtain a consistent and meaningful result, it is critical to prepare high-quality, well-characterized reactive composites. In this project, we are targeting for the synthesis of reproducible metal-dispersed reactive composites including Al-dispersed in Teflon, Ammonium Nitrate (AN) and Ammonium Perchlorate (AP). Here, we describe the synthesis of high quality Al-Teflon composites in Figure 1.

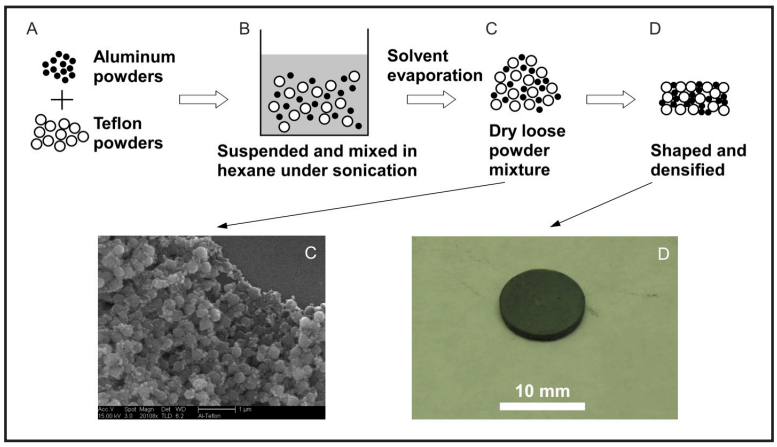

Figure 1: Preparation of Al (120 nm) dispersed in Teflon (200 nm).

We used three different sizes of Al nanoparticles (50, 80 and 120 nm in diameter with a few nm oxide layers, made by a short-pulse plasma process) and Teflon nanoparticles (~200 nm in diameter). These particles

have tendency to clump together, resulting in highly irregular heterogeneous mixtures. Therefore, we mixed and sonicated these particles in hexane (Fig. 1b) and, then, evaporated hexane to produce homogeneously dispersed powder mixtures (Fig. 1c). Then, the mixtures were cold-sintered to a small pellet (~10 mm in diameter and 1 mm thick) of Al-teflon composite (Fig. 1d) using a hydraulic press. The composites were prepared with three Al/Teflon ratios (70/30, 50/50 and 30/70), each with four packing densities (0.3, 0.5, 0.7, and 0.9) for systematic investigations.

Time-dependent data of thermal, chemical, and mechanical properties of high explosives are critical to obtain in-depth insights of shock initiation and detonation [2–4]. The temperature is by far the most important thermodynamic variable controlling the physical and chemical changes of shock-compressed high explosives in many regards [5]. For example, it is the most sensitive probe for the energy balance of chemical reactions. Both the rate and pathway of chemical reactions vary significantly with temperature, typically following an exponential dependence. Importantly, high temperature resulting from exothermic chemical reactions is one of the main driving forces leading to high explosive detonation. However, it is often a challenge to determine temperature, especially the evolution of temperature from detonating explosives in real time, because of highly transient and energetic nature of shock initiation and detonation. For this reason, detonation temperatures have typically been calculated in many cases by using various thermochemical models [6-7] of which results need to be validated experimentally.

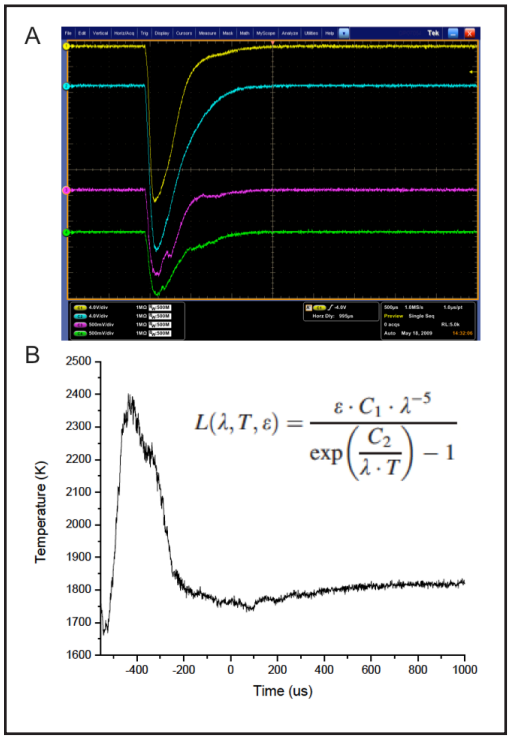

Figure 2: Time resolved temperature of Al-teflon composite: (a) as determined on the PMT; and (b) converted to temperatures by fitting the (a) to the grey body formula in the inset.

Therefore, we have examined a feasibility of measuring time-resolved temperatures of blasting Al-Teflon composites. Our results were quite promising as shown in Figure 2. We used a short-pulse laser (Q-switched, 10 ns Nd:Yag laser pulse at 532 nm) to ignite Al-teflon composites, and the temperature were determined by fitting the measured thermal emission to a gray-body radiation formula [8]. A six-channel optical fiber was used to collect and deliver thermal emission from the sample to a spectropyrometer system which consists of six sets of photomultiplier tubes (PMTs), narrow beam pass filters, and neutral density (ND) filters. The PMTs were set at six discrete wavelengths centered at 340, 400, 450, 506, 598, and 700 nm (340 and 400 nm are not shown in Fig. 2a), each with a full band-pass width of 50 nm. The PM tube outputs were optimized to be about 100 mV by using an appropriate set of ND filters and were recorded at a gigahertz sampling rate on three four-channel digital scope analyzers (DSAs) at various vertical sensitivities. Prior to the actual laser ignition, the entire system (including the sample assembly, optical fiber, PMTs, etc.) was calibrated against a known black-body radiation source, which correlates the DSA vertical outputs to the spectral radiance. These calibrated DSA outputs were then fitted to a gray-body radiation equation at every one-microsecond time step, providing one microsecond time-resolved temperature data for about 2 ms—long enough for the blast event of interest. In this study, we assume that the emissivity is independent of wavelength. The time-resolved data shows that the blasting Al-teflon composite undergoes a wide range of temperature change, ranging from the peak temperature of 2400 K to a steady burning temperature of 1850 K. Importantly, the present optical pyrometric system is good for a faster ns time resolution within the optical window of a few ms (limited by the sampling number points of the DSA). We will continue the time-resolved temperatures of laser-blasted Al-teflon composites, as

well as Al-AN and Al-AP composites using a similar method in Figure 1 with a faster time resolution (1-10 ns).

B.2. Pressure-induced Phase and Chemical Transformations in PETN

Mechanical issues associated with the state of stress, microstructure, grain boundary, heterogeneity, etc., are all very important to understand shock initiation and detonation in high explosives [9-10]. It is well known that PETN exhibits a strong orientation dependence of its initiation and detonation under shock compression [11-12]. Aimed at gaining the insights into shock sensitivity, we have investigated PETN under quasi-hydrostatic and non-hydrostatic conditions. The results are shown in Figure 3.

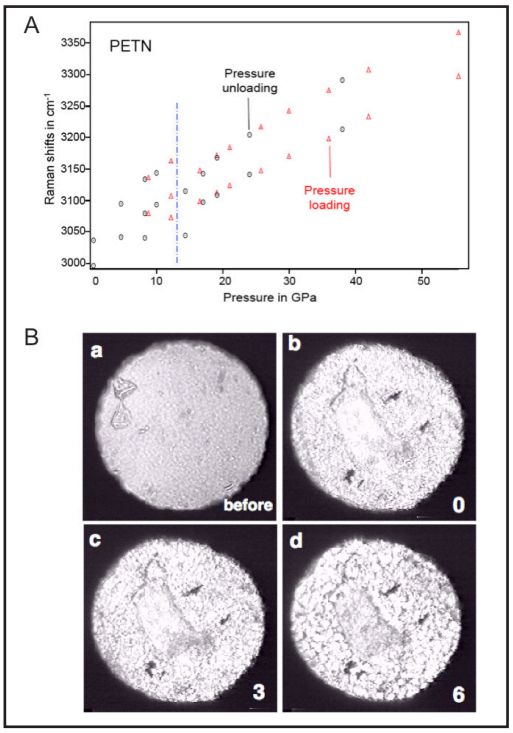

Figure 3: (a) Pressure-induced Raman shifts of PETN in hydrostatic Ar pressure medium, showing a phase transition at ~12 GPa; and (b) photographic images of PETN in non-hydrostatic condition, showing an abrupt chemical reaction at 10 GPa.

Figure 3a plots the pressure-induced shifts of C-H vibrational Raman peaks of PETN to 50 GPa in an Ar pressure-transmitting medium. Soft Ar provides a quasi-hydrostatic condition in this pressure range. The plot clearly shows an abrupt peak shift at ~12 GPa, which occurs reversibly upon the pressure cycling. In contrast, nonhydrostatically compressed PETN behaves completely differently and shows the evidence for chemical decomposition at ~10 GPa. Figure 3b shows the microphotograph images of PETN taken before and after the chemical reaction at 10 GPa and ambient temperature. Note that the reaction occurs rapidly (within a frame time of CCD camera, <30 ms) and exothermically (evident from the sudden movement of small Ruby particles at the gasket edge shown in the frame (a) and produces black carbon particles over a time scale of several seconds (noted in each frame in s). This reaction is probably related to an increase in shear with increasing pressure. Chemical reactions in non-hydrostatic conditions have been observed previously in nitromethane [13], HMX [14] and 1,4-dinitrocubane [15], all of which can be considered broadly as a shear-induced chemical reaction. The hydrostatic data, on the other hand, indicates no apparent chemical reactions, but a structural phase transition at 12 GPa—a similar pressure associated with chemical decomposition.

In order to understand the relationship between the structural phase transition and the chemical reaction, we now investigate PETN in dynamic-diamond anvil cell (*d*-DAC), which can produce well-controlled pressure, compression rates, and dynamic shear strains [16], coupled with time-resolved spectroscopic methods [17, 18].

C. 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 H_2O_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 Li_2O_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.

Year 5:

- Made significant progress on Al dispersed Teflon, especially in preparation of high-quality reactive composites and time-resolved temperature measurements of laser-ignited reactive composites.
- Investigated high-pressure behaviors of pentaerythritol tetranitrate (PETN) under quasi-hydrostatic and non-hydrostatic conditions.

D. Milestones

Our major research accomplishments are on the investigation of phase and chemical stabilities of energetic materials under both static and dynamic high PT conditions. The accomplishment realized in static conditions included the following efforts:

- Mapped out the phase diagram and melting/decomposition curves of the two most commonly used nonconventional energetic materials: ammonium nitrates (AN; published in *Journal of Chemical Physics* 2011, 2012 and 2013) and ammonium perchlorates (AP; published in *Journal of Chemical Physics* 2016).
- Determined crystal structures, phase transitions, and chemical stabilities of Group I alkali metal peroxides including H_2O_2, Li_2O_2 and Na_2O_2 under static high pressures (published in *Journal of Chemical Physics* 2008 and 2017).
- Investigated static high-pressure properties of triaceton triperoxide (TATP)—the explosive used in the recent terrorist attacks in Paris and Brussels—in collaboration with Project R1-C.2 University of Rhode Island (URI). The URI group (led by Professor Oxley) have provided the sample, and we have examined the phase and chemical stability of TATP under high pressures, using micro-Raman spectroscopy and synchrotron X-ray diffraction.
- We have investigated high-pressure behaviors of pentaerythritol tetranitrate (PETN) under quasi-hydrostatic and non-hydrostatic conditions. PETN is one of the most powerful explosives in use today and is known to exhibit highly anisotropic shock sensitivity

The accomplishments realized in the dynamic conditions included the following efforts:

- Developed Time-Resolved synchrotron X-ray diffraction (TRX), TR Spectroscopy (TRS), and TR Pyrometry (TRP) for studies of reactive materials. These technologies are capable of probing structural and chemical evolutions of energetic materials subjected to dynamic thermal and mechanical ignitions as

described in several publications in *Review of Scientific Instruments* (2012), *Journal of Applied Physics* (2012), and *Journal of Materials Research* (2012).

- Performed TRX experiments on reactive metal composites including Ni and Al composites with boron, nitrogen, AN, and AP, using the nation's brightest hard X-ray source at the Advanced Photon Source (APS). The results have provided quantitative information on the chemical and structural evolution of reactive materials undergoing metal combustions, intermetallic reactions, and thermite reactions. The main findings of this work will be submitted to *Journal of Applied Physics* (2018).
- Developed a synthetic method of high-quality, well-characterized metal-dispersed reactive composites including Al-dispersed Teflon, AN and AP, and a short pulse laser ignition experiment for fast (ns) time-resolved temperature measurements.

E. Future Plans (Year 6)

As a result of the ALERT Biennial Review conducted in March of 2018, this project has been concluded and will not be funded in Year 6. As much as possible, we will complete the investigations currently in progress with the following specific objectives:

- Continue to complete the work on TATP under static high PT conditions.
- Determine the dynamic responses of nitromethane and PETN in d-DAC, coupled with TRS.
- Investigate the dynamic responses of metalized explosives (Al-dispersed Teflon, AN and AP), subjected to the laser ignition, using our TRS and TRP capabilities.
- Publish the major findings from the experiments listed above.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

The present project provided 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.

B. Related Basic Science Needs for Materials in Extreme Conditions

Our project addressed 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 (<1 μg)" 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.

C. 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 Lawrence Livermore National Laboratory (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 measure fast time-resolved temperatures of detonating explosives.

D. Data and/or IP Acquisition Strategy

Fundamental data describing: (1) Thermal and chemical stabilities, and (2) chemical kinetics and energetics of high impact explosives, was produced in this project and then used to develop and/or validate the relevance chemical models used in CHEETAH 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 peer-reviewed processes and for a greater level of distribution.

E. 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.

F. 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 Los Alamos National Lab (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, Minseob Kim, on fundamental research programs related to DHS and DoD needs.

B. Peer Reviewed Journal Articles

Pending-

1. Minseob Kim, Jesse Smith, Ross Hrubiak, and Choong-Shik Yoo. “Thermochemical reactions of Al-based intermetallic composites to AlN.” *Journal of Applied Physics*. Submitted for publication.

C. Student Theses or Dissertations Produced from This Project

1. Duwal, S. "Chemistries of Hydrogen-Sulfur Compounds, Layered Materials and Nitrogen-rich Azide Under High Pressures." Ph.D. in Chemistry, Washington State University, May 6, 2018.

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