

SYMPOSIUM H

Multifunctional Energetic Materials

November 28 - 30, 2005

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* Invited paper

8:30 AM *H1.1

Reactive Nanocomposite Powders: Synthesis by Arrested Reactive Milling and Characterization. Edward L. Dreizin, Mirko Schoenitz, Mikhaylo Trunov, Swati Umbrajkar, Xiaoying Zhu, Salil Mohan and Vern Hoffmann; Mechanical Engineering, NJ Institute of Technology, Newark, New Jersey.

Recent progress in synthesis and characterization of reactive nanocomposite powders produced by Arrested Reactive Milling (ARM) will be described. In ARM, the mechanical milling of reactive components is interrupted just before a self-sustaining exothermic reaction is mechanically triggered. The products are micron-sized powders in which each particle comprises a fully dense composite of reactive components mixed on the nano-scale. These materials are of interest for explosives, pyrotechnics, and propellants. Both a shaker mill and a planetary mill were used to produce new energetic nanocomposite materials. A methodology has been developed to produce 2 - 4 pounds per day while eliminating handling of dry reactive powders which may be pyrophoric and exhibit high ignition sensitivity. A wide range of thermite compositions and reactive nanocomposites were produced including those capable of gas release accompanying their reaction. The specific compositions include $2\text{Al}+\text{MoO}_3$, $2\text{Al}+3\text{CuO}$, MgH_2+2CuO , $3\text{MgH}_2+2\text{MoO}_3$, $2\text{Al}+\text{Bi}_2\text{O}_3$, $3\text{Zr}+2\text{Bi}_2\text{O}_3$, $\text{B}+\text{Ti}$, $2\text{B}+\text{Ti}$, $\text{B}+\text{Zr}$, $\text{Si}+\text{CuO}$, etc. Custom-made milling vials capable to withstand high pressure were used to work with the compositions producing gas as a result of reaction. The synthesis conditions have been systematically varied to affect the scale of mixing between the reactive components. In particular, the time of milling, the ball to powder mass ratio, the amount of process control agents, and the density of the grinding media were varied. In addition, the processing temperature was controlled using custom-made heat sinks to cool the milling vials and employing an air conditioner added to a commercial planetary mill. The structure, stability, and oxidation behavior of the produced materials were characterized using electron microscopy, x-ray diffraction, and thermal analysis. Ignition kinetics was determined using an experiment in which a layer of powder was coated on an electrically heated filament and ignited at different heating rates and in controlled gas environments. Emission spectra and flame temperatures produced by reaction of a range of nanocomposites were measured using a fiber optics spectrometer. Specific results for selected material systems will be described and discussed in detail.

9:00 AM H1.2

Synthesis and Characterization of Dual Functional Energetic Structural Materials. Roussislava Zaharieva and Sathyanaraya Hanagud; Aerospace Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Binary energetic materials are of significant interest to the energetic materials community because of their capability to release a significant amount of heat during a chemical reaction and their relative insensitivity. Intermetallics like Ni and Al or mixtures of metal fuel (Al) and oxidant (iron oxide) are some of the candidate binary energetic materials. The current interest is to synthesize these binary energetic materials with appropriate binders, reinforcements and gas-phase materials to produce dual functional energetic -structural materials. These dual functional materials can provide strength when desired and release energy when needed. In this paper, we describe the synthesis and characterization of a dual functional material consisting of aluminum and nickel, with different types of binders and reinforcements. Specifically, the work focuses on intermetallic powder mixtures of Ni-Al with the addition of carbon fibers at micron level, or CNT at nano level, as reinforcements, and epoxy and/or Teflon, Estane, HTPB or PBAN, as binders. These mixtures are synthesized by mixing, partially curing and pressing to obtain desired densities, followed by a complete curing process. Reinforced versus non-reinforced mixtures, and micron-sized versus nano-sized powders, are compared. The reaction temperature is studied under thermal loading in DTA, and the reaction products are analyzed by X-ray diffraction. Scanning electron microscopy is used to characterize the microstructure of the pressed specimens. Strength characteristics are determined using compression tests, tensile tests and Charpy impact tests. The dynamic characteristics are obtained using gas gun tests.

9:15 AM H1.3

Novel Energetic Composite Materials. Jun Nable and Andrew Sherman; Powdermet Inc., Euclid, Ohio.

A new powder metallurgical manufacturing route is developed to produce novel high energy reactive composite that can also perform structural functions. These energetic materials will be fabricated by

depositing a metallic coating onto the particle core as a method to control mechanical properties and reaction kinetics. These reactive metal matrix composites can be developed to offer optimum performance with specific strength while providing controlled release of energy.

9:30 AM *H1.4

Reactive Multilayer Foils for Structural Energetic Applications. Timothy Weihs, ¹Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; ²Reactive NanoTechnologies, Hunt Valley, Maryland.

Multilayer foils that react exothermically are a relatively new class of materials that are now entering commercial and military applications as rapid sources of energy. Given these materials are fully dense and at least partially metallic, they can also serve a structural function in addition to an energetic function. This presentation will review our ability to model and control the thermo-mechanical properties of these new structural/energetic materials based on their chemistry and the characteristics of their layering. Ignition requirements, reaction velocities, reaction heats, foil strengths, and foil stiffnesses will be discussed and comparisons of model predictions and experimental measurements will be offered. Results from vapor-deposited multilayers that measure 10 to 200 microns in thickness and from cold-rolled foils that measure 50 to 500microns in thickness will be discussed.

10:30 AM H1.5

Self-assembled Ordered Energetic Composites of CuO Nanorods and Nanowells and Al Nanoparticles with High Burn Rates. Rajesh V. Shende¹, Senthil Subramaniam¹, Steve

Apperson¹, Shameem Hasan¹, Shantanu Bhattacharya¹, Yuanfang Gao¹, Maruf Hossain¹, Shubhra Gangopadhyay¹, Paul Redner², Deepak Kapoor² and Steven Nicolich²; ¹Electrical and Computer Engineering, University of Missouri, Columbia, Missouri; ²U.S. Army, ARDEC, Picatinny, New Jersey.

Recently developed nanoenergetic materials have attracted wide attention due to their superior performance in terms of higher propagation rates or energy release. Currently, these are synthesized by either mixing fuel nanoparticles with oxidizer nanoparticles or by adding fuel nanoparticles to an oxidizer gel. A drawback of both these synthesis methods is that they lead to microstructural heterogeneity, which in turn reduces interfacial surface area and decreases the propagation rates. According to the published literature, $\text{Fe}_2\text{O}_3/\text{Al}$ nanoparticle mixture indicates a burn rate of 550m/s, whereas for sol-gel derived, it increases to 900m/s in a confined environment. The combustion mechanism in solids is conduction type, whereas for the porous gel, convective combustion generally dictates higher propagation rates. If the diffusion path and interfacial boundary layer resistance for a thermite reaction are reduced and if higher reaction enthalpy is chosen, we believe that it should be possible to achieve very high burn rates. This could be achieved by synthesizing self-assembled ordered structure of oxidizer and fuel. In ordered structures, it is expected that the combustion wavefront propagating at higher rates should generate shock waves similar to those produced by primers and thus, they will serve as green primary explosives. Two kinds of self-assembled ordered nanoenergetic composites have been synthesized. In one, Al-nanoparticles were self-assembled around CuO nanorods and in the second, CuO nanowells were impregnated with Al. CuO nanorods were synthesized by a crystal growth method using suitable precursors. These nanorods (about 10×70 nm) when mixed with Al nanoparticles (80 nm) showed burn rates of 1800m/s as compared to 500m/s for the CuO nanoparticles/Al. Self-assembly was achieved by developing a monolayer of a polymer around the nanorods which had bonding sites for both CuO and Al particles. The TEM image revealed that Al nanoparticles were arranged in an orderly manner around CuO nanorods in the self-assembly and this resulted in increase in burn rate to 2300 m/s. CuO nanowells were synthesized using surfactant templating and nucleation. The surfactant was removed by annealing the samples at 400 C. The chemical composition of these nanowells was confirmed by FTIR and their microstructure was studied using TEM. CuO nanowells (about 25×2000 nm), were dispersed with Al nanoparticles in 2-propanol to prepare a nanoenergetic composite. However, in this method, the size of Al was a limiting factor for reduced diffusional path and interfacial separation. In another method, Al nanoparticles were coated with the surfactant and self-assembled to form a corona of the micelles, and around these micelles oxidizer nanowells were nucleated. The burn rate of this composite was about 2500m/s, which is the highest self-propagation rate observed to date. The shock wave associated with a combustion wavefront was confirmed using a piezoelectric sensor.

10:45 AM *H1.6

Low Density Metals Through Combustion Synthesis. Bryce Tappan, Los Alamos National Lab, Los Alamos, California.

The synthesis of low-density, nano-porous materials has been an active area of study in chemistry and materials science dating back to the initial synthesis of aerogels. These materials, however, are most often limited to metal oxides, e.g., silica and alumina, and organic aerogels, e.g., resorcinol/formaldehyde, or carbon aerogels, produced from the pyrolysis of organic aerogels. The ability to form monolithic metallic nanocellular porous materials is difficult and sometimes elusive using conventional methodology. Here we report a relatively simple method to access unprecedented ultra-low-density, nano-structured, monolithic, transition-metal foams, utilizing self-propagating combustion synthesis of novel transition-metal complexes containing high nitrogen energetic ligands. During the investigation of the decomposition behavior of the high-nitrogen transition metal complexes, it was discovered that nanostructured metal monolithic foams were formed in a post flame-front dynamic assembly having remarkably low densities down to 0.011 g cm⁻³ and extremely high surface areas as high as 270 m² g⁻¹. We have produced monolithic nano-porous metal foams via this method of iron, cobalt, copper and silver metals. We expect to be able to apply this to many other metals and to be able to tailor the resulting structure significantly.

11:15 AM *H1.7

The Application of Energetic SHS Reactions in the Synthesis of Multi-functional Bone Tissue Engineering and Drug Delivery Systems. John Jeremy Moore¹, Doug Burkes¹, Reed Ayers¹, Guglielmo Gottoli¹, Hu Chun Yi² and Jacques Guigne²; ¹Metallurgical and Materials Engineering, Colorado School of Mines, Golden, Colorado; ²Guigne Space Systems Inc (GSSI), Golden, Colorado.

The term combustion synthesis, or self-propagating high temperature synthesis (SHS), refers to an exothermic chemical reaction process that utilizes the heat generated by the exothermic reaction to ignite and sustain a propagating combustion wave through the reactants to produce the desired product(s). The products of combustion synthesis normally are extremely porous: typically 50 percent of theoretical density. Advantages of combustion synthesis over traditional processing routes, e.g., sintering, in the production of advanced materials such as ceramics, intermetallic compounds and composites include process economics, simplicity of operation, and low energy requirements. However, the high exothermicity and rapid combustion propagation rates necessitate a high degree of control of these reactions. One research area being conducted in the Institute for Space Resources (ISR) at the Colorado School of Mines (CSM) is the application of combustion synthesis (SHS) to synthesize advanced, engineered porous TiB-Ti, NiTi, NiTi-TiC, TiC-Ti and multiphase/heterogeneous calcium phosphate (HCAp) for bone tissue engineering and drug delivery systems. Such material systems require a complex combination of properties that can be truly classified as multi-functional materials. The range of properties includes: an overall porosity of 40-60% with a pore size of 200-500 nm; mechanical properties (compression strength and Young's modulus) that match those of natural bone to avoid stress shielding; and a surface chemistry that is capable of facilitating bone growth and mineralization. The paper will discuss the synthesis of porous TiB-Ti, NiTi, NiTi-TiC, TiC-Ti and multiphase/heterogeneous calcium phosphate (HCAp) for bone tissue engineering and drug delivery systems.

11:45 AM H1.8

Reactive Binary Al-Li Powders Prepared by Mechanical Alloying. Xiaoying Zhu, Mirko Schoenitz and Edward L. Dreizin; New Jersey Institute of Technology, Newark, New Jersey.

Mechanically alloyed (MA) powders in the Al-Li binary system with the composition Al_{0.7}Li_{0.3} are synthesized as potential fuels for propellants and explosives. The objective of this project is to compare ignition and combustion characteristics of the mechanically alloyed Al-Li powders to those of aluminum powders of similar size. The synthesized materials as well as intermediate samples recovered from different milling times are studied by x-ray diffraction (XRD). The AlLi intermetallic phase is readily produced by mechanical alloying but disappears after extended milling times. The final product is a solid solution of Li in Al in which the Al crystal structure is preserved while the crystal lattice parameter is changed because of the dissolved Li. Relaxation of the metastable mechanically alloyed material upon heating and its oxidation behavior are studied using differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) up to a maximum temperature of 1500C. For reference, DSC traces are also measured for pure Al and Li powders as well as for corresponding Al-Li powder blends. Possible correlations are analyzed between the oxidation behavior and phase transformations occurring in the mechanically alloyed Al-Li powders heated in oxygen and argon, respectively. Oxidation steps observed are identified; partially oxidized powders are quenched and their phase compositions are studied using XRD. It is observed that the mechanically alloyed powder heated in inert environment exhibits three relatively weak

exothermic reactions between 150C and 430C, and two endothermic reactions, around 540C and 600C. The only equilibrium transition expected based on the binary Al-Li phase diagram is the eutectic melting of Al-AlLi, occurring around 600C. When the alloy was heated in dry oxygen, five relatively sharp and pronounced exothermic peaks were observed to occur between 350C up to 700C; each exothermic peak was accompanied with significant weight increase. Further work, including analysis of the structure and composition of quenched samples, ignition and combustion experiments and their correlation with the thermal analysis data will be discussed.

SESSION H2: Synthesis and Processing II

Chair: Reed Ayers

Monday Afternoon, November 28, 2005

Room 301 (Hynes)

1:30 PM *H2.1

Linear Cellular Alloys in Lightweight Steels and Composites: Fabrication, Quasi-static and Dynamic Properties.

Joe Cochran¹, Justin Clark¹, David McDowell^{2,1}, Thomas Sanders¹ and Naresh Thadhani¹; ¹Materials Science and Technology, Georgia Institute of Technology, Atlanta, Georgia; ²Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Linear Cellular Alloys (LCAs) of ~25% relative density were fabricated by extrusion of oxide powder mixtures into honeycomb structures with widely ranging cell geometries. The oxide extrusions were hydrogen reduced to the alloy and sintered to near theoretical density in the cell walls. Compositions presented for this study include Maraging steel and Super Invar, both FeNiCo based alloys. These chemo-powder processed alloys compared well to wrought alloys when porosity is taken into account. Metal honeycombs fabricated using the powder processing technique have been shown to perform near or above levels predicted by available models. Out-of-plane behavior was consistent with existing models for yield strength and mean crushing strength. The overall performance of the triangular LCA showed good energy absorption due to high plastic buckling strengths and plateau strengths. Energy absorption values ranging from 49 to 140 J/cc have been achieved from LCAs. Dynamic behavior of LCAs was investigated for applications such as energetic capsules or penetrators. Epoxy was used to simulate the mechanical response of energetic filler. Two capsule designs were tested in quasi-static compression with multiple alloy and fill conditions. Dynamic testing was accomplished using a reverse Taylor anvil impact test to achieve strain rates greater than 6000 s⁻¹. Quasi-static compression testing showed improved yield strengths for filled samples as compared to pure epoxy samples. Energy absorption was significantly improved as well. The presence of the epoxy altered the mode of failure of the LCA by preventing buckling and collapse consistent with cellular materials. Barreling and splitting of cell walls was predominant for the ductile LCA material, while fracture and shearing was seen in the brittle materials. Dynamic testing showed that by encapsulating the energetic filler in a cellular material such as an LCA, the pressures generated in the capsule could be increased by a factor of 3 at the same velocity and a factor of more than 5 at higher velocities. Further, fragmentation of the capsule system provides an additional element of shear that could aid in initiation of the energetic reaction. The LCA alloy may also be tailored to control fragmentation as well by altering cell size and wall thickness. While the compositions tested are likely not suitable for penetrator applications, the LCA provides added stability to the system by increasing the dynamic strength.

2:00 PM *H2.2

Polymer-Coated Ultra-Fine Particles. Patrick Brousseau¹ and Charles Dubois²; ¹Energetic Materials, DRDC Valcartier, Val-Belair, Quebec, Canada; ²Department of Chemical Engineering, Ecole Polytechnique de Montreal, Montreal, Quebec, Canada.

Ultra-fine metallic particles have demonstrated recently their potential in tailoring the performance of energetic materials. However, it is generally accepted that they are currently used as nanometric ingredients in macroscopic mixes, and that the optimal way to exploit their properties would be to create intimate interactions between them and the surrounding medium at the nanometer scale. DRDC Valcartier has recently explored methods to create controllable nanometric coatings on metallic particles and has opted to use polymers to treat the particles. Those coatings can have multiple positive effects. For example, in the case of aluminium, small particles are very reactive and tend to cause interactions with the surrounding media. One example is the ageing of aluminium nanoparticles in the presence of air and humidity. Ultra-fine particles age much faster than micron-size particles. The long-term stability of energetic material mixes containing ultra-fine particles will be affected by this reactivity, and coatings would help to solve this problem. Another example is the interaction of aluminium nanoparticles with nitramines that causes

gasing. Three coating methods will be presented: by thermoplastics using a Ziegler-Natta reaction, by thermosets through a polycondensation reaction initiated at the surface of the particles, and in-situ coating of particles by on-line polymerization during the plasma production of powders. The results of coating experiments using those methods will be presented. To assess the performance of the coating methods, ageing tests were carried out on coated and uncoated nanoparticles. The results of ageing tests with those methods will be presented and compared. It will be shown that the polymer coatings reduce significantly the loss of active metal content during accelerated ageing tests. The potential for these coating methods to create different energetic materials by placing more reactive coatings on the particles will also be presented. Since the purpose of the powders is to be used in energetic materials, a study on the rheological effects of the coated particles on polymeric solutions will be presented as well. Finally, future applications of the powders will be discussed.

3:30 PM *H2.3

Product design of particulate energetic materials.

Ulrich Teipel¹, Ulrich Foerter-Barth² and Michael Herrmann²;

¹Particle Technology, University of Nuremberg, Nuremberg, Germany; ²Energetic Materials, Fraunhofer Institute for Chemical Technology, Pfünz, Germany.

The crystal quality and the internal microstructure of crystals have a great influence on the sensitivity of energetic materials. Besides, the particle size and the particle size distribution are of great importance to the processing technology of energetic materials. Particle properties can especially be influenced by applying different crystallization techniques, such as cooling crystallization, membrane crystallization, emulsion crystallization and others. The goal of the investigations was to determine the interrelationship between the properties of the gained crystals and the process parameters. Special attention was directed to the qualitative and quantitative examination of crystal defects and their dependence on the experimental conditions. Besides, the morphology and structure of crystals were calculated by molecular modelling. The effect of crystal defects on the sensitivity of the material was tested on different collectives of particles having varying amount of crystal defects.

4:00 PM H2.4

Control of the Structural Refinement in Al-MoO₃ Nanocomposites Prepared by Arrested Reactive Milling.

Swati M. Umbrajkar, Mirko Schoenitz and Edward L. Dreizin; Mechanical Engineering, New Jersey Institute Of Technology, Newark, New Jersey.

This project is part of the main research effort aimed to develop new reactive nanocomposite materials for applications in enhanced blast explosives, pyrotechnics, reactive structural materials, and propellants. The reactive nanocomposite powders are prepared by Arrested Reactive Milling (ARM). When a blend of powders capable of a sufficiently exothermic reaction is ball-milled, this reaction is triggered mechanically after a certain time. In ARM, metastable nanocomposites with high energy density are formed as a result of arresting (or stopping) the milling process prior to the initiation of such a spontaneous reaction. The objective of this paper is to determine the range in which the degree of structural refinement can be changed in a controlled way and how such refinement affects reactive properties of the produced materials. Previously, thermite compositions in the Al-MoO₃ system were studied and reported to be of interest to practical applications. Based on those earlier results, the stoichiometric 2Al+MoO₃ thermite composition was selected for this project. Altering the milling parameters led to different refinement in the structure of the produced nanocomposites. Specifically, four different types of milling media with different densities, namely steel, alumina, zirconia and tungsten carbide were used to achieve different energies of collisions. Experiments were conducted using a Spex 8000 shaker mill. In addition to the density of the milling media, the amount of process control agent (PCA) and the milling times were varied. The number of balls used during the milling was kept constant, hence the ball to powder mass ratio and the impact energy imparted to the sample from the ball to ball and ball to wall collisions changed in a well-controlled fashion. X-ray diffraction, electron microscopy, and thermal analyses were used to characterize the prepared materials. In addition, ignition tests using an electrically heated filament were conducted. Preliminary results indicate a clear effect of density of the grinding media on the crystallite size of the prepared nanocomposites. Ignition experiments show that the ignition temperatures decrease for the powders with higher degree of structural refinement. Further experimental results will be presented and discussed in detail.

4:15 PM H2.5

Synthesis of Branched Phosphazene Based Energetic Materials. Barny William Greenland¹, Joachim Steinke¹, David Widdowson¹, Peter Golding² and Steve Trussell²; ¹Chemistry

Department, Imperial College, London, United Kingdom; ²AWE, Aldermaston, United Kingdom.

Hyperbranched polymers offer opportunities for high levels of functional groups combined with tuneable solution and solid state properties, compatible with large scale synthesis and bulk polymer production costs. Also, hyperbranched polymers, like their perfectly 3-dimensionally branched cousins, the dendrimers, offer reduced solution viscosities, broadened solubility windows and lower glass transition temperatures amongst other interesting features.[1] They have found use in fields as diverse as supports in solid phase synthesis, surface coatings, homogeneous catalysis and gene delivery agents; but to the best of our knowledge they have yet to find application in the field of energetic materials.[2] Our focus in this regard is on new materials based on phosphazene chemistry. Particularly the use of cyclotriphosphazenes as a highly functional structural motif in hyperbranched polymer synthesis. Selective modification of a hexachlorophosphazene building block generated AB_x-type monomers which were subsequently polymerised into a hyperbranched prepolymer for the in situ introduction of energetic groups. Similarly we explored the alternative A6 and B2 comonomer system to form a hyperbranched [cyclomatrix] prepolymer which underwent further modification to form new energetic materials. In addition to molecular characterisation data we will present the effect of functional group loading, the degree of branching and molecular weight in relation to T_g and energetic performance. In order to accurately model the likely properties of these new materials we designed and synthesised a family of cyclophosphazene containing dendrimers, the first ever made by the convergent route. Members of the family retained the same basic structure but differed in surface group loading levels, allowing precise structure/energy content relationships to be drawn.

4:30 PM *H2.6

Mechanically Alloyed Al-based Materials. Huey Hoon Hng, School of MS&E, Nanyang Technological University, Singapore, Singapore.

Metals such as Al, B, Mg, etc. have high combustion enthalpies and are considered as prospective energetic materials for propellants, explosives and pyrotechnics. Currently, aluminium is most widely used in the high energy density formulations. The advantages of aluminised fuels are their high oxidation enthalpy, high combustion temperature, environmentally benign products, and relatively low cost. However, it is widely recognized that the benefits expected from these metal powders are not fully exploited, mostly due to its long ignition delays, high ignition temperatures, incomplete combustion and slow combustion rates, partly attributed to the passivation of aluminium surface. Several approaches have been reported to accelerate the ignition rate and, hence the combustion rate, such as using metastable alloy nanopowders. One practical way to synthesize metastable alloys is mechanical alloying in a high-energy ball mill. This technique has been used by many researchers to produce unusually high supersaturated solid solutions, intermetallic phases and even in-situ reactions in raw materials that are apparently mutually inert to each other under normal conditions. High-energy ball milling leaves the powder in a state of non-equilibrium so that, when an opportunity is provided, the transformation kinetics will be triggered to attain equilibrium by reaction or phase change releasing energy. In this study, various Al-based alloys (e.g. Al-Mg and Al-Fe alloy systems) prepared by mechanical alloying via planetary high-energy ball milling have been studied. Different milling processing parameters, namely process control agent (PCA) and ball-to-powder ratio (BPR), were investigated. The structural and morphology changes during the milling process were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The thermal properties were characterized using differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). Here we report our findings and propose possible relationships between the microstructures and properties of these mechanically alloyed materials.

SESSION H3: Characterization
Chair: Patrick Brousseau
Tuesday Morning, November 29, 2005
Room 301 (Hynes)

8:15 AM *H3.1

Ultrafast Dynamics of Nanotechnology Energetic Materials. Hyunung Yu, Selezion A. Hambir and Dana D. Dlott; School of Chemical Sciences, University of Illinois, Urbana, Illinois.

Energetic materials containing nanometer dimension materials are a topic of great interest at the present time. The microscopic mechanisms of these nanoenergetic materials has been studied in our laboratory using a picosecond flash-heating method. A variety of techniques are used to probe the dynamical behavior of materials

containing Al and B nanoparticles combined with several different kinds of oxidizers. These techniques include vibrational spectroscopy, absorption spectroscopy, emission spectroscopy and time-resolved microscopy. Together these techniques permit the determination of the detailed mechanism of nanoenergetic material performance with high time and space resolution.

8:45 AM **H3.2**

On-Chip Initiation and Burn Rate Measurements of Thermite Energetic Reactions. Steven Apperson¹, Shantanu Bhattacharya¹, Yuanfang Gao¹, Senthil Subramanian¹, Shameem Hasan¹, Maruf Hossain¹, Rajesh V. Shende¹, Shubhra Gangopadhyay¹, Paul Redner¹, Deepak Kapoor² and Steven Nicolich²; ¹Electrical and Computer Engineering, University of Missouri, Columbia, Missouri, Missouri; ²U.S. Army, ARDEC, Picatinny Arsenal, Picatinny, New Jersey.

Existing methods to measure burn rates of energetic reactions require expensive imaging systems and significant amounts of the bulk material. We developed a novel on-chip method to measure burn rates of energetic material. In our on-chip method, we used Pt thin films on glass substrate for initiation and burn rate tracking, and then painted a dispersion of thermite (oxidizer/fuel) material over the films. On ignition, as the reaction propagated, the change in resistance of Pt film was monitored in a LabView program via high-speed data acquisition hardware. The burn rate of the energetic reaction was obtained from the propagation distance traveled and measured time of propagation. The change in resistance was due to alloy formation. This was confirmed using scanning electron microscopy and x-ray diffraction technique. Using this method, we measured burn rate of CuO/Al and Fe₂O₃/Al nanoenergetic materials in 1 m/s to 3000 m/s range. The validity of our measurement system was established by comparing the results of similar samples available in the literature. High voltage and expensive systems like semiconductor or metal bridge wires are currently available for on-chip initiation of energetic reaction in primary explosives. We have developed an on-chip heater/thermite initiator that can be operated by a low voltage power supply for initiation of patterned thermites. This initiator creates shock waves that can be used directly for the detonation of high explosives, hence eliminating the need for primers. This initiation mechanism works due to hot-spot density dispersion, which creates maximum energy localization necessary for effective initiation. For these initiators, a voltage source of 3-30 V was used to supply power to the thin-film heater, and the heater was fabricated to have a resistance of about 0.5 -1 Ohm. The initiation time was controlled in millisecond to microsecond range by controlling the supplied power and properties of the thermites. Our on-chip initiator can be further improved, through modification of the fabrication, to allow multi-point initiation system using current MEMS technology. Currently, we are pursuing efforts to improve the on-chip system further so it can measure all aspects of performance and sensitivity of the material. The performance includes initiation temperature, reaction temperature, detonation velocity, and blast pressure. The sensitivity requirements include impact, friction, and electrostatic discharge sensitivity of the energetic materials. Overall, the on-chip method is simple, rapid, inexpensive, and safe, and these attributes make this technique effective for both diagnostic and initiation purposes.

9:00 AM ***H3.3**

Overview of Nanoscale Energetic Materials Research at Los Alamos. Steven F. Son, Lawrence Livermore National Laboratory, Livermore, California.

Novel properties associated with nanostructured energetic materials have attracted a great deal of interest recently. Metastable Intermolecular Composite (MIC) materials are comprised of a mixture of oxidizer and fuel with particle sizes in the nanometer range. They can have high energy densities and exhibit fast combustion velocities. These properties make them very attractive in a number of applications, including lead-free primers and igniters. In this paper I will present an overview of recent efforts at Los Alamos to characterize and better understand the reaction mechanisms of these advanced energetic materials.

9:30 AM **H3.4**

Protocols for in vitro toxicity screening of aluminum nanoparticles. Maria Palazuelos^{1,4}, David Moraga², Brij Moudgil^{1,3}, Mick Popp² and Kevin William Powers¹; ¹Particle Engineering Research Center, University of Florida, Gainesville, Florida; ²Interdisciplinary Center for Biotechnology Research, University of Florida, Gainesville, Colorado; ³Materials Science and Engineering, University of Florida, Gainesville, Colorado; ⁴Department of Chemical Engineering, University of Florida, Gainesville, Florida.

The growing development and use of particulate materials for energetic materials applications demands a better understanding of the possible effects and mechanisms of interaction of these materials

with biological systems. In this study we have paid special attention to the full characterization of the aluminum particulate systems tested. Well-characterized nanoparticulates were then used in exposure studies to evaluate their in vitro effects at the cellular level. The potential reactivity of nanoaluminum powders in-vitro is of particular significance. Several biological endpoint assays (LDH release, metabolic activity and apoptosis) were conducted as indicators of cell death, cell proliferation and cell viability. Electron microscopy was also used to study morphology and fate of the cells in the exposed cells. The cell line selected for these experiments is the human lung carcinoma A549 (type II alveolar epithelial cells). Several relevant sizes and shapes of nanoaluminum were evaluated including spherical aluminum powders (Nanotechnologies) and aluminum flake of nanoscale thickness (Sigma Technologies). Titanium oxide nanopowders (Degussa P25 and NanoTek) and Crystalline quartz (Min-u-sil 5) were evaluated as positive and negative controls. The materials were well dispersed and characterized for size, surface properties, and morphology. Concentration and time courses were designed in order to evaluate the extent of cytotoxicity, and to define critical conditions for further research. Treatment consisted of exposing the cells to particles in culture for time periods ranging from 4 to 72 hours and in concentrations from 30 µg/ml to 500 µg/ml. Bioassays were run following standard procedures as outlined in the instructions provided with kits (Roche Diagnostics and BioSource). All measurements were obtained using appropriate controls in order to minimize artifacts such as light scattering by the particles themselves. Electron Microscopy shows that the particles were up taken by the cells and engulfed in lysosomes. The results from the bioassays indicate that different nanoparticulate materials in different concentrations can have significant effects on cell health. The aluminum and quartz caused the highest cytotoxicity measured by LDH released. These biological endpoint tests have allowed us to identify conditions under which phenotypic differences can be observed due to exposure to aluminum nanopowders. Such information is being used along with microcalorimetry and differential gene analysis studies (microarray) in order to gain further understanding of the mechanisms of interaction between nanoparticles and various cell lines.

10:15 AM ***H3.5**

Understanding and Tuning the Reactivity of NanoEnergetic Materials. A. Prakash, A. Rai, A. McCormick and Michael R. Zachariah; University of Maryland and NIST, College Park, Maryland.

Nanostructured fuel/oxidizer composites are being looked upon as a possible approach to enhance energy release rates. Here we report on some aspects that make nanoparticles with reactivities different than bulk. We use these ideas to explore methods to tune reactivity. We report on two approaches to moderate/tune reactivity. In the first example we accelerate reactivity. The method is based on electrostatically enhanced assembly to promote the preferential arrangement of aluminum (fuel) nanoparticles with iron oxide (oxidizer) nanoparticles in the aerosol phase. Two unipolar chargers are employed to generate oppositely charged aluminum and iron oxide particles, which enhance the formation of intimately interconnected nanocomposite energetic materials. The results of burning tests and thermal analysis using differential scanning calorimetry (DSC) showed that aluminum/iron oxide nanocomposite aerosol materials synthesized by bipolar assembly had burning rates that are a factor of 10 higher than those produced by random Brownian coagulation. In a second approach we employ a very reactive oxidizer (Potassium permanganate; ~150 nm) and create a less reactive shell (Iron oxide). The measured reactivity for a nano-Al/composite oxidizer could be varied by more than a factor of 10 as measured by the pressurization rate in a closed vessel (Psi/microsecond), by changing the coating thickness of the iron oxide. The composite oxidizer nanoparticles were synthesized by a new aerosol approach, where the non-wetting interaction between iron oxide and molten potassium permanganate aids the phase segregation of a nanocomposite droplet into a core-shell structure.

10:45 AM **H3.6**

Substrate Effects in Electrical Initiation of Nanolaminate Thin Films. Joseph W. Tringe, Alexander E. Gash and Troy W. Barbee; Chemistry & Materials Science Directorate, Lawrence Livermore National Laboratory, Livermore, California.

Nanolaminate thin films can release energy to perform useful functions, such as welding and heating. For most applications the films are attached to a thick substrate, which plays an important role in determining the heating rate and maximum attainable surface temperature of the film/substrate system. Here we demonstrate that nanolaminate films on substrates can be initiated by joule heating. In these electrically initiated films, the substrate is critical for defining the energy and time needed to start the chemical reaction among nanolaminate layers. We describe experiments performed with

Ni(V)Al nanolaminate/substrate systems, varying nanolaminate thickness and substrate material. Current-voltage characteristics of the films are obtained during electrical initiation, from which the time and energy of initiation are obtained. We model the heat transfer processes associated with the initiation event, and use these calculations to predict the effect on initiation time and energy, of varying the nanolaminate and substrate thickness, as well as varying the substrate thermal conductivity.

11:00 AM *H3.7

Inorganic Nanoparticles for Gun Propellants.

Barbara Baschung, ISL, Saint-Louis, France.

The possibility of increasing the burning rate of rocket solid propellants by adding nanoparticles of aluminum into the propellant formulation has been already well-known for many years. This paper deals with nano- and micron -particles embedded in gun propellants. The objectives are to increase the gun performance and to reduce the erosion of the weapon barrel. The burning behavior of solid propellants based on ultra-fine aluminum powder was investigated at a high pressure range which is reached in a gun tube. The burning rate of such propellant is much higher (nearly two order of magnitude) than for the similar propellant with the micron-size aluminum. Further this paper presents a review of burning experiments with propellants based on the nano- and micron-size particles of metal and oxide components (such as Al, TiO₂, BN). Burning behavior of NENA solid propellants based on nano-scale aluminum were studied as a function of the portion of aluminum in the mixture. The burning of these propellants follows Vieille's burning law. The burning rate increases by increasing the aluminum portion in the propellant. Theoretical models are reviewed to understand these experimental burning results. In the outlook an advanced propellant coated with appropriate nanoparticles is presented. With this propellant and an especially ignition by microwaves it shall be possible to ignite solid propellants by high loading densities (> 1.2 g/cm³).

11:30 AM *H3.8

Energy Release Characteristics of Impact-Initiated Energetic Materials. Richard G. Ames, Naval Surface Warfare Center, Dahlgren Division, Dahlgren, Virginia.

Impact-initiated energetic materials are a class of energetic materials that are formulated to release energy under dynamic loads. Under quasi-static loads, however, the materials are inert and carry a classification of 4.1 flammable solid. In general, these materials are formed by introducing a metal powder (or powders) into a polymer binder. The materials are sufficiently insensitive so as not to produce a self-sustaining reaction; as such, they require the mechanical work of a high-strain rate plastic deformation process to provide the energy required to drive the reaction. Traditional initiation techniques such as exploding bridge wires or flame initiation are not sufficient to maintain a reaction in these materials. The Naval Surface Warfare Center, Dahlgren Division (NSWC-DD) has been investigating these materials for a variety of applications. A primary focus in this investigation has been in understanding the relationship between material properties and the corresponding strength and reactivity for a given material. A number of novel diagnostic techniques have been developed in order to quantify the energy release characteristics of the materials, including an impact-initiated energetic material test chamber. This test chamber differs from traditional bomb calorimetry techniques in that it captures the energy release that is associated with the dynamic impact process. Results from this test effort have shown that there is only a weak correlation between theoretical energy densities and measured energy release. It is postulated that this discrepancy is a result of the dominance of material strength properties in the initiation and propagation of a reaction. NSWC-DD has also been conducting a modeling and simulation effort. It is the aim of this effort to relate the meso-scale properties of the material constituents (e.g. metal particle size and density) to the continuum properties of the composite material (e.g. dynamic strength). This relationship is essential because it defines the link between the formulation parameters and the engineering requirements: the requirements are placed on the continuum properties of strength and reactivity whereas the materials are formulated at the meso-scale level of particles size and density. Because this relationship is unknown it is difficult to engineer materials to meet specific requirements. This paper will present a description of the energy release testing techniques, results for a broad array of material types, and comparison between the theoretical and measured energy densities. It will also present an overview of the meso-scale modeling approach, including the methods used to investigate phenomena such as dynamic material strength and initiation. It will conclude by recommending future work to be conducted to address gaps in the current understanding of the relationship between impact-initiated energetic material properties and their mechanical and energy release behavior.

SESSION H4: Mechanisms I

Chair: Randall Simpson

Tuesday Afternoon, November 29, 2005

Room 301 (Hynes)

1:30 PM *H4.1

The Effect of Nanopowder Attributes on Reaction Mechanism and Ignition Sensitivity of Nanothermites. Jan A. Puszynski, Christopher Bulian and Jacek J. Swiatkiewicz; SD School of Mines and Technology, Rapid City, South Dakota.

Nanothermite composites have several properties that are not typical of conventional thermites. The nanoscale size of the individual reactants is responsible for the significant differences in these properties. Several different thermite mixtures are investigated to characterize these properties. These systems include Al-Fe₂O₃, Al-CuO, Al-MoO₃, and Al-Bi₂O₃. Several previous studies have reported on the behavior of these mixtures during unconfined burning and on the characterization of particle attributes such as particle size, surface area, and reactive metal content. This study is focused on several other attributes. Electrostatic discharge is an important factor in the accidental ignition of certain nanothermite mixtures. Experiments were performed to quantify the electrostatic nature of the powders and to mitigate the electrostatic sensitivity through the use of particle coating. The nanoscale nature of the thermite components also has an effect on the kinetics of the reaction. Differential scanning calorimetry is used to determine activation energy of the systems. Several experimental setups are used to monitor the nanothermite mixtures during combustion. The mixtures are monitored during combustion in small diameter tubes using high speed video technology and a pressure sensor system. These tests are used to characterize combustion propagation under confined conditions and determine the effect of pressure and mixture density on propagation rate. Experiments are also performed using both a closed volume pressure cell and recoil force cell to measure the reactive power of the mixtures.

2:00 PM H4.2

Aluminum Activation Mechanisms. Curtis E. Johnson, Timothy J. Foley and Kelvin T. Higa; Research Department, NAVAIR, China Lake, California.

This study involves an investigation of the mechanism of activation of aluminum toward oxidation by inorganic additives. Metal fuels are used in energetic material formulations to boost energy content and performance. The full potential of metal fuels has not been realized due to slow kinetics that result in incomplete combustion in the desired time frame. The oxidation and combustion of aluminum particles can be promoted with the addition of certain inorganic compounds, including metal fluorides and metal oxides. Sodium hexafluoroaluminate (cryolite) has shown activating effects on aluminum combustion and oxidation in several laboratory tests, including thermite and intermetallic reactions, benchtop powder burning experiments, and thermogravimetric analysis experiments in air. However, in some combustion tests no activating effect is observed, and it is not yet clear whether cryolite activation will be effective in an energetic material application. An understanding of the mechanism of the activation process should allow one to assess the potential utility of the activating agents. The oxidation of nano aluminum powders in air was characterized by variable temperature x-ray powder diffraction and thermogravimetric analysis. For a 33-nm aluminum powder the aluminum oxide produced by air oxidation was poorly crystallized until the sample was heated to above 1050C, where the alpha-alumina phase crystallized. For a mixture of the aluminum with cryolite, crystallization of oxide phases is enhanced, with Na-Al-O phases evident at 550C and above. Fluorine is lost from the sample between 550 and 850C, presumably due to reaction with moisture to produce HF. In a similar experiment with aluminum and silver molybdate, the only crystalline product was alpha-alumina, which was observed at 550C and higher. The activating agents act in part by altering the chemistry and crystallization of the oxide product from aluminum oxidation.

2:15 PM H4.3

Ignition of Aerosolized Reactive Particles at High Heating Rates. Salil Mohan, Yuriy L. Shoshin and Edward L. Dreizin; Mechanical Engineering, New Jersey Institute of Technology, Newark, New Jersey.

This paper presents an experimental methodology and initial results describing ignition of rapidly heated, aerosolized powders of different materials. The experimental setup uses a focused 125 W CO₂ laser (Synrad E125) as a heating source. A thin laminar aerosol jet of reactive particles is fed into the laser beam through a small nozzle from a plate capacitor in which the powder is aerosolized using a technique called electrostatic particulate method. The velocities of particles are in the order of 0.2 to 1 m/s and are measured using a

modulated green laser sheet focused on the particle jet and a video camera (Panasonic PV-GS35) recording the particle streaks. The setup enables the experiments to be conducted in different gaseous oxidizers. The laser power is increased until the particles are observed to ignite. The ignition is detected optically. The ignition threshold is measured for particles of different sizes. The size distributions for the powders are determined using low-angle laser light scattering. The results of measurements are processed to determine the ignition temperatures and activation energies for different materials. For justification of the experimental technique, a series of tests were conducted with spherical magnesium powders for which the ignition activation energy is relatively well known. Two different fractions with different particle sizes were used in the study, ranging between 3 to 50 microns. Further experiments were performed with aluminum and several recently developed aluminum-based mechanical alloys. Experimental methodology and initial results will be presented and discussed.

3:30 PM *H4.4

The effect of slow heating rates on the reaction mechanisms of nano and micron composite thermite reactions.

Michelle L. Pantoya and John J. Granier; Mechanical Engineering Dept, Texas Tech University, Lubbock, Texas.

Nano-thermite reactions have shown unique properties in ignition sensitivity and deflagration (flame propagation) speeds which have propelled thermites to new realms of applications. The decrease in required ignition stimuli of nano-thermites is an improvement for many payload critical applications, but the ignition sensitivity also creates various hazards during material handling and seems to be a factor in decreased reactivity of aged nano-thermites. This work will outline results from differential scanning calorimetry experiments on aluminum (Al) and molybdenum trioxide (MoO₃) nano-thermite reactions as a function of Al particle size and heating rate. Experiments were designed to examine a range of Al particle sizes from 50 nm to 20 microns mixed with nano-scale MoO₃ at heating rates ranging from 2.5 to 15 C/min. Measurements record ignition temperatures, peak temperatures, heat of reaction and a Kissinger analysis is used to calculate apparent activation energy. Results show that the nano-thermite reactions initiate prior to Al or MoO₃ phase changes and at least 300 C below similar micron-thermite reactions. The difference in ignition temperature is suggestive of unique diffusion mechanisms in nano versus micron thermite reactions. Nano-thermites also display higher heat of reaction values that are consistently dependent on experimental conditions (i.e., heating rate). Optimum apparent activation energies (in terms of minimum ignition energy requirements) are shown for the largest nano and smallest micron thermites, indicating that a minimum activation energy exists and is a function of Al particle diameter.

4:00 PM *H4.5

Evolution and Revolution - Changing Energetics Technology.

Adam S. Cumming, Energetics Technology, DSTL Fort Halstead, Kent, United Kingdom.

In the past different groups worked on specific aspects of energetic materials, with little contact amongst themselves or with users of the technology. As a result opportunities were often missed and advances were either duplicated or not fully understood in the broad context. The result was a technology seen as pedestrian and mature and thus requiring little investment, with few opportunities for real research. In the last ten years this situation has changed, though not the perception of the users etc. New species have been produced for application, and novel molecules proposed, but in addition new, or rather different, ways of using the technology have been developed or imported. It has been claimed that the Fall of Constantinople in 1453 drove much of the Renaissance in Europe, and in the same way access to Russian developed technology has contributed to a reconsideration of what we thought we knew. At the same time new computing tools made the modelling of events and processes accessible, and propellant and explosives scientists were thrown together, producing new thoughts and questioning old certainties. Thus a combination of new technology; access to different processes and assumptions, and the interaction of disparate groups have produced what should become a new, multifunctional approach to the science and technology. This paper will discuss the threads weaving the new tapestry, and consider how the pattern can be developed and optimised to meet the needs of the technology users in the next decades. In addition it will discuss how those user demands can be shaped by the new opportunities offered by the revolution and renaissance now taking place, and finally, how to make those users aware of the opportunities becoming available.

4:30 PM H4.6

Study of Melting and Oxidation of Nanometer Size Aluminum Powders. Swati M. Umbrajkar, Mikhaylo Trunov, Mirko Schoenitz and Edward L. Dreizin; Mechanical Engineering, New

Jersey Institute Of Technology, Newark, New Jersey.

Recently, nanometer-sized aluminum powders became available commercially and their use as potential additives to propellants, explosives, and pyrotechnics has attracted significant interest. It has been suggested that very low melting temperatures are expected for nano-sized aluminum powders and that such low melting temperatures could accelerate oxidation and trigger ignition much earlier than for regular, micron-sized aluminum powders. The objective of this work is to investigate experimentally the melting and oxidation behavior of nano-sized aluminum powders. Powder samples with three different nominal sizes were provided by Nanotechnologies Inc. The nominal average sizes of these powders were 40, 80, and 120 nm. Melting of these materials was studied by differential scanning calorimetry where the powders were heated from room temperature to 700 °C in argon environment. Thermogravimetric analysis was used to measure the mass increase while the powders were heated in an oxygen-argon gas mixture from room temperature to 1500 °C. The phase compositions for the oxidized samples were determined from x-ray diffraction analysis. The measured melting curves were compared to those computed using the experimental particle size distributions and a thermodynamic model describing the melting point as a function of the particle size. The melting onset temperature predicted theoretically correlated reasonably well with that observed experimentally. Characteristic step-wise oxidation was observed, with the formation of different transition alumina polymorphs detected by x-ray diffraction. The mass increase of these powders during oxidation up to 1500 °C was measured. Based on the mass increase, the initial oxide layer thickness was estimated to be in the range of 3.0 nm to 3.5 nm for these powders. However, no correlation was found between the melting and oxidation of the aluminum nanopowders. The observed oxidation behavior was interpreted considering the recently established kinetics of oxidation of micron-sized aluminum powders.

4:45 PM H4.7

Combustion Mechanisms of Nanocomposite Al/PTFE.

Dustin T. Osborne and Michelle L. Pantoya; Mechanical Engineering Dept, Texas Tech University, Lubbock, Texas.

This study examines the unique reaction behaviors associated with a polytetrafluoroethylene (PTFE) binder and nanometer scale aluminum (Al) particles compared with micron-scale Al particles. Reactive mixtures of Al and PTFE rely on thermal degradation of the fluoropolymer to produce fluorinated gases that oxidize aluminum. While heating nano-Al combined with PTFE in air with different weight percentages of PTFE, a transition from slow deflagration to thermal explosion was observed when PTFE content increased from 30% to 40%. To explore the causes of this transition, DSC and TG analyses were performed in an argon environment on the mixtures revealing a two-stage reaction process after the decomposition of PTFE. The exothermicity of the first stage of the reaction process does not change with additional PTFE content; however, the exothermicity of the second stage appears to be a strong function of PTFE content, increasing exponentially as PTFE content increases. The DSC/TG results explain the Al/PTFE reaction mechanism and offer insight into the transition from deflagration to detonation observed in bulk samples. Thermokinetic analyses are used to propose a theory for the unique reactions associated with nano-scale particles. These results are useful for the safe handling and use of binder containing energetic material formulations.

SESSION H5: Poster Session
Tuesday Evening, November 29, 2005
8:00 PM
Exhibition Hall D (Hynes)

H5.1

Density of RDX Crystals Grown During High Acceleration in an Ultracentrifuge. Mary Y. D. Lanzerotti¹, Richard Z. Squillace¹,

Alex Gandzelko¹ and Jagadish Sharma²; ¹U. S. Army ARDEC, Picatinny Arsenal, New Jersey; ²Carderock Division, Naval Surface Warfare Center, West Bethesda, Maryland.

We report studies of the density of RDX (cyclotrimethylene-trinitramine) crystals grown during high acceleration (high *g*) in an ultracentrifuge. When a RDX saturated acetone solution is accelerated at 200,000 *g*, the RDX solute molecules move individually through the acetone solvent molecules to form a RDX crystal because the density of the RDX (Theoretical Maximum Density 1.806 g/cc) solute is more dense than the acetone (0.79 g/cc) solvent. Crystal growth is controlled by the *g*-force. Crystal defects including voids and solution inclusions caused by temperature variation or evaporation at 1 *g* are minimized. A nitrogen pycnometer was used to measure the density of the RDX crystals grown at 1 *g* and at 200,000 *g* for 120 hours. The density of the RDX (1.7980 g/cc)

crystals grown at 200,000 g is greater than the density of RDX (1.7881 g/cc) crystals grown at 1 g.

H5.2

Theoretical and Experimental Study of the Vibrational Spectroscopy of 2,4-Dinitroimidazole. Jennifer A. Ciezak and Samuel F. Trevino; ARL/NIST, Gaithersburg, Maryland.

The vibrational spectra of 2,4-Dinitroimidazole were measured at 15K by inelastic neutron scattering at the NIST Center for Neutron Research. Direct analysis of the measured spectra was accomplished using ab initio density functional theory for both an isolated molecule and a crystalline solid. Comparison of the observed and computed INS spectra revealed that the solid-state calculations provide a better description of the experimental INS spectrum and clearly demonstrate the power of this combined experimental/theoretical approach.

H5.3

Assessment of Deposition and Clearance Fractions using the ICRP 66 Lung Model for Airborne Nanomaterials.

Charles Jenkins¹, Jorge Hurtado², Wesley E. Bolch² and Chang-Yu Wu¹; ¹Dept. of Environmental Engineering Sciences, University of Florida, Gainesville, Florida; ²Dept. of Nuclear and Radiological Engineering, University of Florida, Gainesville, Florida.

The focus of this research is to assess the deposition and clearance fractions associated with the inhalation of nanoparticles from residues produced by the detonation of explosives or their initial component ingredients. Such a study is important because of several reasons, including (1) toxicity of heavy metals; (2) the adverse health effects due to nanoparticles even for those non-toxic when in bulk; (3) inhalation is the most vulnerable route for human beings as the defense mechanisms in the lungs are not robust for nanoparticles. Deposition and clearance estimates from data presented will be used to generate statistical distributions for inhaled nanoparticles. The deposition model based on the ICRP 66 report has been programmed through the use of a computer code entitled the Lung Dose Uncertainty Code, or LUDUC (Bolch et al. 2001). This newly revised lung model defines each compartment within the respiratory tract, as well as providing variations in particle deposition and clearance from previous reports. With the ability to use codes based on the ICRP 66 respiratory tract model, deposition fractions and clearance fractions were calculated. Deposition fractions take into account both the shape and average diameter of the nanoparticles observed. Due to the small average diameter of the nanoparticles simulated, a deeper particle deposition was observed. Due to the depth of deposition within the respiratory tract, it was observed that the clearance times for these particles with a slow nanoparticle solubility rate into surrounding tissue and extra cellular fluids were on the order of weeks. Combining deposition and clearance observations results in a first step toward understanding the mechanical processes involved with nanomaterials within the respiratory system.

H5.4

Atomistic Simulations of PETN Molecular Nanocrystalline Particles. Theodore Golfopoulos¹, Longguang Zhou¹, Hanchen Huang¹ and Richard H. Gee²; ¹Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York; ²Chemistry and Chemical Engineering Division, Lawrence Livermore National Laboratory, Livermore, California.

Pentaerythritol tetranitrate (PETN) - a molecular crystalline energetic material - has performance properties that are intricately related to the crystallite particle size and morphology. Further, it is well known that these crystalline particles coarsen with time, leading to a decrease of effective surface area, and therefore changes in the material's overall performance properties. Here we perform atomistic simulations based on empirical force fields to investigate the coarsening mechanisms, particularly molecular transport on and incorporation near surface sites. This study spans over several surface configurations, including high symmetry flat surfaces, surface steps, and ridges separating surface facets. We find that diffusion is favored along the close-packed (110) plane, although important secondary movement occurs on the (001) surface. However, our data show that the energetics of the diffusion process is dependent not only upon the crystallographic surface, but also upon the features of the surface landscape. These results are valuable in that they provide insight into our understanding of the underlying mechanisms associated with PETN nanocrystalline coarsening. The work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

H5.5

New Approach for Large-Scale Production of Carbon Single-Walled Nanotubes: Synthesis of Small Diameter Nanotubes. E. Mora¹, T. Tokune² and A. R. Harutyunyan²;

¹Physics Department, The Ohio State University, Columbus, Ohio;

²Honda Research Institute, Columbus, Ohio.

The great potential of carbon single-walled nanotubes (SWNTs) in different applications is limited by the inability to produce large and homogeneous quantities. Typical production rates reported for continuous production of SWNTs are less than 1 g h⁻¹, after purification. Here, we report a new technique with higher production rates, up to 6 g h⁻¹ after purification, and scaling capability up to 220 g h⁻¹. The SWNTs are produced by vertical floating technique and continuous injection of pre-prepared supported catalyst powder. The carbon product formed is pushed away from the reactor by a gas stream and collected in two consecutive collectors and a trap. These collectors were designed based on the concept of cyclone separators. The main advantage of our method is the use of previously synthesized catalyst that consists of metal particles (Fe/Mo), with suitable diameters for the growth of SWNTs, embedded in a support powder (Al₂O₃). Our approach solves the important problems presented by other techniques concerning catalyst particle diameter and concentration, as well as the formation of undesired carbon forms caused by pyrolysis of surfactants. More importantly, there are no conceptual or technical restrictions for industrial scale up using our method. High injection rates of up to 40 g h⁻¹, corresponding to a production yield of pure SWNTs of 6 g h⁻¹, were achieved. The samples collected in the different containers were characterized using Raman scattering, transmission electron microscopy and thermogravimetric analysis under air (TPO). The Raman spectra of the sample collected from the trap suggested that only narrow distribution of SWNTs diameter (0.8 to 1.2 nm) exists. Meanwhile, the spectra corresponding to samples from container 1 and container 2 indicate a wide distribution of diameters (0.8 to 2 nm). Furthermore, according to the TPO results, the carbon content of the as-prepared product varied in the soot collected from container 1, container 2 and trap, with the corresponding carbon yields of ~15, 8 and 5 wt. %, respectively. Moreover, varying the gas flow rate into the reactor changed the Fe catalyst content of the resultant samples. Therefore, we believe that the product was separated in situ depending on the synthesis duration and, in this manner, by diameter distribution. This unique characteristic of our synthesis method opens opportunities to produce small diameter SWNTs and study their growth mechanism. The results also indicate that nucleation of SWNTs with smaller diameters occurred first during the synthesis. We explain this interesting observation by assuming that the carbon-induced liquefaction of small particles occurs earlier than in bigger ones, due to their lower melting point [1,2]. [1] A. R. Harutyunyan, E. Mora, T. Tokune, Appl. Phys. Lett., 86, 153113, 2005. [2] A. R. Harutyunyan, E. Mora, T. Tokune, Appl. Phys. Lett., accepted June, 2005.

H5.6

Patterning PETN and HMX using Dip Pen Nanolithography.

Omkar A. Nafday^{1,2}, Brandon L. Weeks¹, Jason Haaheim² and Ray Eby²; ¹Chemical Engineering, Texas Tech University, Lubbock, Texas; ²Sales and Applications, NanoInk Inc., Chicago, Illinois.

Recently there has been a focused effort to develop reliable nanoscopic writing and reading capabilities. Dip-pen nanolithography TM (DPNTM) has emerged as a convenient method to deliver nanoscale materials onto a substrate by leveraging scanning probe microscopy capability. In the DPN method, ultra sharp atomic force microscope tips (radius ~ 10-20 nm) coated with chemical compounds are used to deposit the compounds on a suitable substrate to form a stable nanoscale pattern. A new application for the DPN method is the field of nanodetonics which is the nanoscale decomposition and study of reactions of explosives. Deposition of thin films of energetic materials presents a challenging problem because most explosives are sensitive organic molecules that decompose at relatively low temperatures. In contrast, methods such as thermal evaporation and sputtering will not work as the explosives will decompose at ambient conditions when preparing thin films. Results will be presented for pentaerythritol tetranitrate (PETN) and high molecular weight cyclotetramethylene tetranitramine (HMX) on gold and silicon substrates at various relative humidity and temperatures. PETN is one of the strongest known high explosives and generally used as a booster for small caliber ammunition or as the explosive core of detonation cords. HMX is used almost exclusively in military applications and also as a solid rocket propellant. The ultimate goal is to pattern both energetic materials in nanoscale registry and investigate their reaction and decomposition at the nanoscale due to heating or shock initiation. In addition to patterning of high explosives, a discussion on the effect of surface energy on patterning rates is investigated. This knowledge will be applicable to inks beyond high explosives.

SESSION H6: Mechanisms II

Chair: Jan Puszynski

Wednesday Morning, November 30, 2005

Room 301 (Hynes)

8:15 AM *H6.1

Shear Localization and Initiation of Chemical Reactions in Energetic Materials Under Dynamic Loading.

Vitali F. Nesterenko^{1,2} and Jing Cai¹; ¹Materials Science and Engineering Program, University of California at San Diego, La Jolla, California; ²Department of Mechanical and Aerospace Engineering, University of California at San Diego, La Jolla, California.

Shear localization is considered as one of the main reasons for initiation of chemical reaction in energetic materials under dynamic loading. However despite of wide spread recognition of the importance of rapid shear flow the shear bands in heterogeneous materials (porous, multicomponent) did not become an object of intensive research. The explosively driven "Thick-Walled Cylinder" method allows to reproduce the array of shear bands with local shear strains 10 - 100 and strain rate 10^7 s^{-1} in practically any materials. Experimental evidence for cascade of shear bands, fracture, vorticity and reaction inside localized shear bands in porous mixtures Nb-Si, Ti-Si, Ti-graphite and Ti-ultrafine diamond was found. Recently Hopkinson bar based "Thick-Walled Cylinder" method was developed to collapse small hollow cylinders (mass about 0.5 g). Different driving media (water, suspension of alumina particles in water, glycerol) were investigated to ensure collapse of hollow cylinders made from polymers and their mixtures with metal particles (PMMA, PTFE, and cold isostatically pressed mixtures of PTFE with Al particles of different sizes (2 and 95 microns), Tin particles, diameter 44 micron under controlled pressure pulse in the set up based on Hopkinson bar. Raman spectroscopy of the samples of the mixture of PTFE and 2 μm aluminum particles demonstrated the evidence of the decomposition/reaction of PTFE inside shear localization area. This phenomenon was not observed under identical conditions of collapse of cylinders made from PTFE, PTFE mixture with Tin and with 95 micron Al particles. Athermal mechanism of shear localization in polymers and reaction initiation is proposed based on experimental results. This work was supported by ONR (N00014-02-1-0491).

8:45 AM H6.2

Shock-Induced Chemical Reactions in Organic Liquids.

Dana M. Dattelbaum, Stephen A. Sheffield, David L. Robbins, Richard L. Gustavsen, Robert R. Alcon, Joseph M. Lloyd and Pete Chavez; Los Alamos National Lab, Los Alamos, New Mexico.

The investigation of shock-induced chemical reactions is essential for understanding and predicting complex processes such as the shock-to-detonation transition in explosives, and the chemical decomposition ("reactants-to-products" chemistry) of organic materials under shock loading. Furthermore, a systematic examination of shock-induced reactions in simple model materials can provide insight into the specific influences of pressure, temperature, and chemical structure on reactivity. Several studies performed previously point to a variety of possible reactions that can occur under shock loading, including dimerization, polymerization, and decomposition, each taking place in different shock-produced pressure and temperature regimes depending on chemical functionality. Here, we present results obtained from single-shock experiments on several carbon and heteroatom (Si and N)-based liquids, in efforts to understand the connections between reactivity and slight changes in chemical structure. Our experiments use a two-stage gas gun to launch a projectile up to 3.4 km/s towards a target containing multiple embedded magnetic gauges that measure the shock profile as a function of Lagrangian position in the liquid. Comparisons of reactivity in carbon vs. heteroatom-based materials and a discussion of relationships between free energy and input shock parameters producing chemical reactions will also be presented.

9:00 AM *H6.3

Hot Spots in Energetic Crystals from Dislocation Pile-up Avalanches. William R. Grise, Department of Industrial and Engineering Technology, Morehead State University, Morehead, Kentucky.

The localized temperature rise at hot spots due to the release of dislocations from a pile-up has been employed to explain both greater drop-weight heights being required to initiate chemical decomposition in smaller sized energetic crystals [1]; and, the susceptibility to shear banding of energetic and referenced inert materials, for example, adiabatic shear banding in steel [2-3]. A revised model to explain adiabatic heating due to release of a pile-up avalanche is put forward here. The model rests on relatively few dislocations in a pile-up, which has been indicated for such energetic crystals as RDX (cyclotrimethylenetrinitramine). The model also represents the resistance of grain boundaries as a thin region with a higher viscosity for dislocation movement than the grain interior [4]. Extensions to the model include the release of concentric circular glide loops forming a pile-up against a grain boundary, and the interactions of such arrays with similar dislocation loop arrays on parallel slip planes [5]. For release from a viscous obstacle, a local temperature plateau occurs in

the thermal response [6] in line with the physical concept of a hot spot. The paper attempts to do two things: (1) make more realistic the pioneering estimates by Armstrong et al. [7] of temperature rises due to pile-up avalanches, and (2) compare and contrast the picture of hotspot heating detailed herein with other important work in this area, e.g., De Hosson, Roos, and Metselaar [8], with their careful assessment of the frictional and drag forces acting on dislocations and the importance of these forces in understanding plastic work by dislocations; and the suggestions by Gilman over the years [9] about the relative importance of moving dislocations as compared to hard-particle bond-breaking as the source of generated heat. References: [1] R.W. Armstrong, C.S. Coffey, V.F. DeVost and W.L. Elban, J. Appl. Phys. 68 (1990) 979; [2] R.W. Armstrong and F.J. Zerilli, Mech. Mater. 17 (1994) 319; [3] R.W. Armstrong, Proc. Eighth Intern. Seminar; New Trends in Research of Energetic Materials, April 19-21, 2005, University of Pardubice, CZ; [4] F.P. Gerstle and G.J. Dvorak, Phil. Mag 29 (1974) 1337; [5] K. Sadananda and M.J. Marcinkowski, J. Appl. Phys. 43 (1972) 2609; [6] W.R. Grise NRC/AFOSR Summer Faculty Fellowship Program, AFRL/MNME, Eglin Air Force Base, FL, 2003; [7] R.W. Armstrong and W.L. Elban, Mat.Sci.&Eng., A122 (1989) L1-L3; [8] J. Th. M. De Hosson, A. Roos, and E.D. Metselaar, Phil. Mag. A 81 (2001) 1099; [9] J.J. Gilman, in CP620: Shock Compression of Condensed Matter - 2001 (2002) 36.

9:30 AM H6.4

Role of Constituent Configuration on Shock-Induced Reactions in a Ni+Al Powder Mixture. Daniel Eakins and Naresh Thadhani; Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Ultra-fast reactions initiated within or immediately behind the shock front in powder mixtures are of importance in the synthesis of high-pressure phases and next-generation energetic materials. Reactions in nickel and aluminum powder mixtures and the establishment of a reaction threshold have been the source of many studies over the last 20 years. Prior work has suggested that the criterion for reaction is most probably mechanochemical in nature, in which shock loading environment plays a larger role than absolute shock energy input. The mechanisms responsible for intimate mixing of fresh reactants are however still unclear. In this work we are investigating the role of particle size and morphology on the loading, mixing, and their subsequent shock-induced reaction behavior, by performing shock-compressibility experiments on equi-volumetric mixtures of nickel and aluminum powders, with variations in nickel particle size (micron and nano-scale) and shape (spherical and flake). Determination of shock states is accomplished through time-resolved in situ PVDF gauge measurements of input shock stress and transit time through the powder mixture. The reaction product shock-compressibility state is also being calculated based on constant pressure (or volume) approximations to allow correlation with measured states for inference of the occurrence of shock-induced chemical reactions. This research is funded through AFOSR/MURI Grant No. F49620-02-1-0382 and by the DoD Graduate Research Fellowship award of Dan Eakins.

9:45 AM H6.5

Dynamic Impact Characterization of Epoxy-Cast Al+Fe₂O₃ Mixtures. Louis Ferranti and Naresh N. Thadhani; Materials Science & Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Dynamic mechanical and reaction properties were evaluated for epoxy-cast Al + Fe₂O₃ powder mixtures using reverse Taylor anvil and parallel plate impact experiments. The investigation is motivated by the need to understand the fundamental behavior of such reactive composite materials subjected to rapidly applied loads involving complex stress states, large strains, and high strain rates experienced particularly during high-speed impacts. In the present work, the samples were prepared using stoichiometric mixtures of commercially available micron-scale aluminum and sub-micron-scale hematite powders. Additionally, mixtures comprised of hematite coated aluminum particles, synthesized by sol-gel processing, were also cast in epoxy. Impact experiments were performed on both types of specimens under similar loading conditions. The dynamic deformation and fracture response of the epoxy-cast samples was captured in real time utilizing high-speed digital photography. Strain, strain-rate, and stress were measured from the captured images. Plate-impact experiments were also performed to determine the P - V/V₀ compressibility. Postmortem microstructural and differential thermal analysis (DTA) of recovered fragments was conducted to determine impact-induced material alteration. The presentation will describe the results of the understanding of the dynamic material response and post-impact chemical reaction changes. Funding for this research was provided in part by AFOSR/MURI under grant No. F49620-02-1-0382; and by a graduate research internship grant (for L. Ferranti) provided by EGLIN AFRL through contract No. F08630-03-C-001.

10:30 AM H6.6

Shear Initiated Reactions in Energetic and Reactive Materials. Denise Meuken¹, M. Martinez Pacheco², H. J. Verbeek¹, R. H. B. Bouma¹ and L. Katgerman^{2,3}; ¹Energetic Materials, TNO Defense Security and Safety, Rijswijk, Netherlands; ²Netherlands Institute for Metals Research, Delft, Netherlands; ³Delft University of Technology, Delft, Netherlands.

Deformation of energetic materials may cause undesired reactions and therefore hazardous situations. The deformation of an energetic material and in particular shear deformation is studied in this paper. Understanding of the phenomena leading to shear initiation is not only necessary to explain for example the response of munitions to intrusions or large deformations imposed in storage accidents. A fundamental understanding of shear initiation also provides the opportunity to initiate energetic materials in a different and controlled manner, and possibly with a tailored reaction rate of the material. Several small and large scale experiments have been performed in which a shear deformation is imposed to high explosives as well as thermite based reactive materials. Experiments are numerically simulated in order to correlate small and large scale experiments and understand the initiation mechanisms. Firstly, the composition PBXN109 (64% RDX, 20% Al, 16% HTPB binder) is studied in the Ballistic Impact Chamber. Steel cylinders filled with this composition have been explosively deformed to different extent. The maximum shear rates involved in the latter experiment are determined with a numerical simulation with the Autodyn hydrocode and compared to shear rates at the moment of reaction as observed with the Ballistic Impact Chamber. Secondly, the effect incorporation of a commercially obtained Insensitive-RDX into a Polymer Bonded eXplosive, as opposed to conventional RDX, is studied. The initiation threshold and reaction type is determined by explosive deformation of steel cylinders with these PBXs as it has been done for the PBXN109. A numerical simulation has been carried out and compared to observed reaction violence of the PBX. Thirdly, the shear initiation of reactive materials of the thermite type is studied by energetic fragment impact and in the Ballistic Impact Chamber. The reactive materials consist of mixtures of nano/micron size particles of aluminium and molybdenum trioxide, eventually mixed with a polymer binder.

10:45 AM *H6.7

Lattice Deformation and Shear Bands Formed in Crystalline Solids by Shock or Impact. J. Sharma and C.S. Coffey¹; ¹ Indian Head Division of NSWC.

Recent Atomic Force Microscope (AFM) observations of shocked or impacted crystalline solids have revealed the presence of substantial lattice deformation and the formation of shear bands. The shear bands were the sites of considerable heating and melting. Three very different materials were examined in detail, the molecular crystal RDX (C₃H₆N₆O₆), gold and silver. For these three materials the shear bands were almost identical in size and shape indicating that the lattice potential had been distorted and overcome by the number density of the moving dislocations responsible for plastic deformation. Large deformations were observed in the crystal lattices of these materials. Significant deformation was also observed in the RDX molecular structure. The spatial resolution of the AFM was about .4 angstroms. These are long lived metastable deformations which have not changed in several years. Our current understanding of these processes will be discussed and the temperatures of the shear bands will be calculated.

SESSION H7: Theory and Modeling
Chair: Jan Puszynski
Wednesday Morning, November 30, 2005
Room 301 (Hynes)

11:15 AM *H7.1

Theoretical Chemical Characterization of Energetic Materials. Betsy M. Rice, Ballistics and Weapons Concepts Division, U. S. Army Research Laboratory, Aberdeen Proving Ground, Maryland.

Our research is focused on developing computational capabilities for the prediction of properties of energetic materials associated with performance, sensitivity or environmental hazard. Additionally, we want to identify and characterize the dynamic processes that influence conversion of an energetic material to products upon initiation. We are attempting to achieve these goals through the use of standard atomistic simulation methods. In this talk, various theoretical chemistry methods and applications to energetic materials will be described. Current capabilities in predicting structures, thermodynamic properties, and dynamic behavior of these materials will be demonstrated. These are presented to exemplify how information generated from atomistic simulations can be used in the design, development and testing of new energetic materials. In addition to illustrating current capabilities, we will discuss limitations

of the methodologies and needs for advancing the state of the art in this area.

11:45 AM H7.2

Atomistic and mesoscale modeling of mechanical and chemical processes in energetic materials. Alejandro Strachan¹, Adri van Duin², William Goddard² and Brad Holian³; ¹Materials Engineering, Purdue University, West Lafayette, Indiana; ²Caltech, Pasadena, California; ³Los Alamos National Laboratory, Los Alamos, New Mexico.

New-generation reactive interatomic potentials with molecular dynamics enable the full-physics, full-chemistry description complex thermal, mechanical, and chemical process in a wide variety of materials. I will describe the use of the first principles-based reactive force field ReaxFF to describe shock and thermal induced decomposition of various molecular energetic materials, including RDX, nitromethane and polyvinylnitrate. Non-equilibrium shock simulations enable the characterization of the initial chemical events under dynamical loading while equilibrium simulations at various temperatures and densities enable us to study phenomena at longer time-scales and follow the reactions to completion. These simulations provide information not only about chemical rates but also a molecular-level understanding of the complex multi-molecular chemistry involved. Furthermore, we find that decomposition time-scales of various materials have a strong correlation with their intrinsic sensitivity to ignition. While providing a very detailed description, all-atom MD simulations are computationally too intensive to simulate many important processes in molecularly complex materials such as shockwaves. Thus, we have recently developed a new mesodynamical method (where a single particle describes groups of atoms) that enables a thermodynamically accurate description of energy transfer between mesoparticles (molecules in this case) and their internal degrees of freedom. We describe the thermal role of the internal degrees of freedom of each mesoparticle using local, finite thermostats that are coupled to the local energy of the mesoparticles. The parameters entering the mesoscopic description can be obtained from all-atom simulations, furthermore the thermal role of the implicit degrees of freedom can be treated with quantum statistics. We exemplify the new method via shock simulations of the crystalline polymer poly(vinylidene fluoride); the mesodynamics results are in excellent agreement with all-atom MD simulations.

SESSION H8: Theory II
Chair: Michael Zachariah
Wednesday Afternoon, November 30, 2005
Room 301 (Hynes)

1:30 PM *H8.1

Atomistic Studies of Fundamental Properties and Processes in Energetic Materials: Relevance to Mesoscale Initiation Phenomena. Thomas (Tommy) D. Sewell, Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

Genuine, physics-based understanding of initiation phenomena in plastic-bonded explosives (PBXs) requires knowledge of the physics and chemistry at mesoscopic scales that are far larger than can be simulated directly using atomistic detail, yet far smaller than is directly resolvable in practical engineering scale continuum simulations. Initiation is determined by localization phenomena that arise due to the heterogeneous character of most explosive formulations. Indeed, the "average" temperature behind a weak shock is not a useful measure for understanding initiation phenomena; rather, it is the tails of the distributions in temperature, stress, and strain rates, localized to small, spatially distributed volumes in the material (hot spots), that dictate the outcome of a given loading event. Important factors for predicting hot spot formation and subsequent extinction or growth/coalescence include particle size, concentration, morphology, and void content; physical and chemical interactions between grains and binder; thermophysical and mechanical properties of the constituents and interfaces between them; and, of course, the inherent chemical stability of the explosive component(s) in the formulation. We are in the process of computing many of the thermophysical and mechanical properties required for a complete specification of constituent models for use in mesoscale simulations, wherein grains and binder in representative volumes of a PBX are spatially resolved and then studied within a continuum hydrodynamic framework. In addition to calculating specific properties of interest, we have recently undertaken a series of large-scale molecular dynamics simulations of energetic crystals to understand dissipation phenomena in dynamically loaded single- or poly-crystalline samples; for instance, plastic deformation and stress/energy localization mechanisms, phase transitions, and so on. Recent and ongoing work in these areas will be discussed, along with

their specific relevance to emerging mesoscale simulation capabilities.

2:00 PM **H8.2**

Characterising and Modelling the Response of Polymer-Bonded Explosives (PBXs) to High-Rate Loading. William G. Proud¹, M. W. Greenaway¹, C. R. Siviour¹, J. E. Field¹, D. Porter², P. Gould², P. D. Church³ and I. G. Cullis³; ¹Physics and Chemistry of Solids Group, Cavendish Laboratory, Cambridge, United Kingdom; ²QinetiQ, Farnborough, Farnborough, United Kingdom; ³QinetiQ, Fort Halstead, Kent, United Kingdom.

Polymer-bonded explosives are being increasingly used as energetic fillings and components in many systems. They are perceived as more chemically and mechanically stable than traditional fillings such as RDX/TNT. They are castable into predetermined shapes, machinable and can be used as structural components. However, along with all these undeniable advantages, as a class, these materials are now undergoing extensive characterisation to ensure they comply with both the legal and technical requirements in energetic systems. It is well-known that polymers display non-linear behaviour and are much more complex than, for example, simple metal systems at any rate of strain. The understanding of PBX systems involves areas as diverse as polymer chemistry, chemical compatibility, mechanical properties, impact tests, thermal stability etc. Predictive modelling of material response is an important aid in this area. This in turn has demanded the application of polymer theory to develop new algorithms to describe the behaviour of these polymer composites. The accuracy of the modelling depends heavily on material characterisation and model validation. The inputs to these models come from a range of experimental measurements from tomography, microscopy, intermediate rate testing (drop-weight) and high-strain rate techniques (Hopkinson bar and plate-impact). This paper will illustrate some of these aspects of material characterisation, using recent studies from the Cavendish Laboratory and QinetiQ as well as other organisations where appropriate. Acknowledgements - The equipment, techniques and views represented in this paper have been developed under funding from a number of organisations including, AWE, QinetiQ, [dstl], EPSRC in the UK and NSWC, ARL, AFRL, EOARD from the USA.

3:30 PM **H8.3**

Shock-Wave Propagation Study in Single Crystalline fcc-Al and γ -Fe₂O₃ and Their Interface Using Classical Molecular Dynamics Simulations. Vikas Tomar and Min Zhou; Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Classical molecular dynamics (MD) simulation is an important technique for analyzing custom-designed nanostructured materials and nano-sized systems such as nanowires and nanobelts. This research focuses on analyzing the shock wave propagation in {100} Al, {110} Al, {111} Al, {0001} Fe₂O₃, and an interface of {100} Al with Fe terminated {0001} Fe₂O₃. A generic potential form is used to describe the behavior of the Fe+Al+Fe₂O₃+Al₂O₃ system for this purpose. The potential is able to describe bulk single crystal behavior of Fe, Al, Fe₂O₃, Al₂O₃ as well as interfacial transitions among them. Shock wave propagation analyses in single crystals with different orientations focus on analyzing the relationship between shock wave velocity (U_s) and particle velocity (U_p) as the orientation is changed. The U_s-U_p relationships obtained agree well with established Los Alamos polycrystalline Rankine-Hugoniot data for both Al and Fe₂O₃. Calculations also focus on analyzing the structural features in the single crystals as the shock wave propagates. With increase in U_p a distinctive change from elastic wave to an overdriven plastic wave is observed in Al. The limits on U_p for this change in wave propagation depend upon crystalline orientation. The shock wave propagation analyses in interface aim at obtaining an account of impedance mismatch at an interface of {100} Al with Fe terminated {0001} Fe₂O₃ during shock wave propagation and its relation with particle velocity. In addition, radial distribution functions at the interface are also analyzed at a range of particle velocities to obtain measure of reaction nucleation at the interface and its relation with the interface pressure and temperature.

3:45 PM **H8.4**

Plastic deformation of semiconducting nanoparticles during a shock wave from first-principles molecular dynamics. Matteo Cococcioni^{1,2}, Gerbrand Ceder^{1,2} and Nicola Marzari^{1,2}; ¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; ²Institute for Soldier Nanotechnology, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The kinetics and thermodynamics of solid-solid phase transformations for group-IV nanoparticles during a shock wave are investigated via first-principles molecular dynamics using a novel electronic-enthalpy functional¹. While nucleation events and basic mechanisms for deformation in Si and larger Ge nanoparticles reveal a strong

similarity with the plastic flow in amorphous Si², significant differences emerge in the plastic and elastic response of the diamond cage under load, dependent both on size and material choice. The potential for nanostructured impact-absorbing materials is highlighted, as is the importance of kinetic effects in determining the adiabatic evolution during the shock.

4:00 PM **H8.5**

Molecular dynamics simulation of shock-induced chemical, mechanical and thermal processes in nanostructured metastable composites. Shijin Zhao¹, Timothy Germann¹ and Alejandro Strachan²; ¹Los Alamos National Lab, Los Alamos, New Mexico; ²Materials Engineering, Purdue University, West Lafayette, Indiana.

Nanostructured metastable intermolecular composites (MICs) are a new class of energetic materials with a wide range of applications. MICs can be made to react to form a more stable compound while releasing a large amount of energy and exhibit several unique properties, for example, extremely fast propagation of the chemical reactions when the initial components are intermixed at the nanometer scales. The fundamental molecular-level mechanisms that govern the unique properties of these materials are to a large extent unknown. We use molecular dynamics to characterize the chemical and mechanical response of Ni/Al nanocomposites induced by shock and thermal loading. We use detailed analysis methods such as the short-range topological analysis to characterize the atomic level processes responsible for the initiation and propagation of the chemical reactions. Our simulations are designed to characterize the role of composition and nanostructure on the initiation and subsequent ultra-fast propagation of chemical reactions in nanostructured MICs as well as their mechanical and thermal properties.