SYMPOSIUM AA

AA: Synthesis, Characterization, and Properties of Energetic/Reactive Nanomaterials

December 1 - 4, 2003

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SESSION AA1: Applications and Toxicology
Chairs: Charles M. Jenkins and Walter Kozumbo
Monday Morning, December 1, 2003
Liberty A-B (Sheraton)

8:30 AM *AA1.1
Potential Usage of Energetic Nano-sized Powders for Combustion and Rocket Propulsion. Kenneth K. Kuo, Grant A. Risha, Brian J. Evans and Eric Boyer; Department of Mechanical and Nuclear Engineering, Pennsylvania State University, University Park, Pennsylvania.

Nano-sized energetic metals and boron particles (with dimensions less than 100 nanometers) possess desirable combustion characteristics such as high heats of combustion and fast energy release rates. Because of their capability to enhance performance, various metals have been introduced in solid propellant formulations, gel propellants, and solid fuels. There are many advantages of incorporating nano-sized materials into fuels and propellants, such as: 1) shortened ignition delay; 2) shortened burn times, resulting in more complete combustion in volume-limited propulsion systems; 3) enhanced heat transfer rates from higher specific surface area; 4) greater flexibility in designing new energetic fuel/propellants with desirable physical properties; 5) nano-particles can act as a gelling agent to replace inert or low-energy gellants; and 6) nano-sized particles can also be dispersed into high-temperature zone for direct oxidation reaction and rapid energy release. A number of facilities at the High Pressure Combustion Laboratory of the Pennsylvania State University have been designed and utilized to characterize the performance enhancement of propulsion systems using nano-particles. For example, several lab-scale hybrid rocket motors have been used as screening devices for selecting appropriate nano-sized particles for propulsion. Hybrid motor data showed that the addition of 13% energetic powders can increase the linear regression rate of solid fuel by 123% in comparison to the unmodified fuel at a moderate gaseous oxidizer mass flow rate. Strand burner studies of two identical solid propellant formulations (one with 18% regular aluminum powder and the other with 9% aluminum replaced by Alex® powder) showed that nano-sized particles can increase the linear burning rate of solid propellants by 100%. In addition to solid fuels and propellants, spray combustion of bipropellants have been conducted using gel propellants impregnated with nano-sized boron particles as the fuel in a rocket engine. High combustion efficiencies were obtained from burning nano-sized boron particles contained in a non-toxic liquid fuel. Materials characterization such as chemical analyses to determine the active aluminum content, density measurements, and imaging using an electron microscope have been performed on both neat nano-sized particles and mixtures containing the energetic materials. In general, using energetic nano-sized particles as a new design parameter, propulsion performance of future propellants and fuels can be greatly enhanced.

9:00 AM *AA1.2
Effects of Very Small Particle Size and Particle Morphology on the Processing and Properties of Energetic Formulations. Robert Wardle, Kenneth Lee, Jeff Akester and Paul Braithwaite; Research and Development Laboratories, ATK Thiokol Propulsion, Brigham City, Utah.

The emergence of nano particles and very fine particle size distributions of existing energetic materials, metal powders and novel compounds, opens doors for an entire new range of formulations. Some of these show different ranges of performance and safety characteristics that are particularly attractive. Along with the attractive characteristics are challenges in processing and the safety characteristics of the very fine powders and intermediate and, occasionally, final compositions. Described in this paper will be several ongoing efforts at ATK Thiokol Propulsion under funding from the ARDEC and internal funding. In this paper, research on novel formulations for explosives and gun propellants will be described. Approaches to deal with the very high reactivity of nano-sized metal powders in an uncoated state will be described. An effective method that has been found is dispersal in a carefully chosen inert solvent followed by in situ precipitative coating with a desensitizing binder dissolved in a dissolved in a dissimilar solvent. The properties of the powders and intermediate and final compositions were carefully measured and will be reported along with selected characteristics regarding the performance characteristics of the final composition. Historically, nitramine based pressed compositions contain particles with a tri-modal distribution including very large (>200 micron) particles to ensure processing. The shock sensitivity of the formulation has always been a compromise between processing requiring larger particles and shock sensitivity for which smaller particles are needed for reduced values. Methods for coating much higher percentages of fine particle nitramine than previously achieved will be described. The inclusion of a much higher percentage of fine particles in a nitramine-based explosive has led to a surprising reduction in sensitivity of the final composition without the normal trade-off of performance for sensitivity. Some unusual aspects of the performance and processing will be reported.

9:30 AM *AA1.3
Energetic Materials R&D at Technanogy Materials Development. Kevin Walter, Chris Aumann, Doug Carpenter and David Pesiri; Technanogy Materials Development LLC, Santa Ana, California.

Recent results from Technanogy Materials Development's superthermite program will be presented.

10:00 AM AA1.4
Strong explosive silicon-based material. Dominik Clement, Dmitri Kovalev, Joachim Diener, Egon Gross, Nicolai Kuenzner and Frederick Koch; Physics E16, TU Munich, Garching, Germany.

We will present porous silicon (pSi) as a new outstanding, highly explosive material completely different from the so far known explosives. Its outstanding position reveals new possible applications e.g. in silicon based high technology. Based on our laboratory measurements we will discuss the dependence of the reaction behavior on the structural properties and the surface termination of the pSi layer, as well as on the atomic ratio of silicon to oxygen and the chosen oxidizer solution. By optical measurements the detonation time was estimated to be faster than 1 μs and the energy output is higher or equal to the strongest explosives known up to now. We report also on other import reaction parameters, as the initial temperature, the pressure development, the propagation speed of the shock wave parallel to the layer surface, and the resulting products depending on the chosen oxidizer solution.

10:30 AM *AA1.5
Characterization of Airborne Ultrafine and Nanometer Particles During Energetic Material Synthesis and Testing. Mengdawn Cheng[1] and Charles M. Jenkins[2]; [1]Environmental Sciences Division, Oak Ridge National Lab, Oak Ridge, Tennessee; [2]High Explosive Reserch Directorate, Air Force Research Lab, Eglin Air Force Base, Florida.

Material when reduced to nanometer scale in one, two, or all three linear dimensions exhibits unusual thermal, electrical, mechanical, and/or optical properties not commonly seen on a larger scale of the same material. Exploration of nanoscale material has gained intense interest recently in a wide range of applications exactly because of the new and unique properties found existing only in nanophase materials. While nanophase materials may contribute significantly to our daily life in the future, their biological behaviors (whether it is beneficial or adversely impacting) have only begun to be known. With the small dimension of nanophase particles, penetration of the particles smaller than 100 nm deep into human lung into alveolar region has been predicted using computer models. Limited experimental data published in the literature and obtained in our own laboratory also indicate that nanoscale particles could be harmful to human health. Selected nanophase materials play a key role in the synthesis and manufacturing of a new generation of advanced energetics. To improve our understanding of the airborne behavior of the nanophase particles in an occupational and a detonation testing environment at the Air Force Research Laboratory, High Explosive Research and Development facility at Eglin Air Force Base, we employ continuous particle measurement instruments and time-integrated filter sampling techniques to collect existing ultrafine and nanometer size particulates. From these samples a number of physical and chemical attributes of the airborne nanoparticles in the above mentioned environments were determined. The data are expected to provide critical information to the protection of workers handling the nanophase material and to design control strategies for minimizing human exposure to the material. We will present the sampling and measurement strategy, and preliminary measurement data to be taken in July 2003.

11:00 AM *AA1.6
Health and Environmental Impacts of Engineered Nanomaterials. Vicki Colvin, Chemistry Dept, Rice University, Houston, Texas.

Nanomaterial synthesis and applications development have reached a point where it is prudent to examine their health and environmental impacts. An overview of this new field will be presented, along with recent results from Rice University's Center for Biological and Environmental Nanotechnology.

11:30 AM AA1.7
Inhalation Toxicology of Ultrafine Particles: Lessons Learned from Studies with PTFE and Al-containing Fumes. Gunter Oberdorster, Environmental Medicine, University of

Rochester, Rochester, New York.

Ultrafine particles (UFP, <100 nm in diameter) are being synthesized for use in numerous applications because of their unique properties, which include a large surface area and small size. They are also formed in very high number concentrations by combustion processes, hence their ubiquitous presence in ambient air. Epidemiological studies suggest an association between inhaled ambient particulate material and adverse cardiopulmonary effects. The mechanisms related to such toxicity, however, are still unclear. We have conducted studies with laboratory-generated UFP-containing fumes (PTFE) elemental carbon, TiO_2 and Al_2O_3 to gain mechanistic information related to UFP toxicity. Specific examples from studies with these UFP will be discussed and how results from those studies may be applied to human exposures and health risks of inhaled nanoparticles.

11:45 AM AA1.8
Preliminary Studies of the Dermal Absorption of Nanoscale Energetic Materials. Stephen M. Roberts, Center for Human and Environmental Toxicology, University of Florida, Gainesville, Florida.

While the dermal penetration of conventional scale energetic materials is generally regarded as insignificant, there is little information on the dermal penetration of energetic materials in nanoscale. Preliminary experiments were conducted to assess the ability of selected nanoparticle energetic materials to penetrate the stratum corneum using skin from hairless mice. Nanoparticles were applied to hairless mouse skin in vitro, both in dry form and in solution. At specified intervals, skin was fixed and sectioned, and the extent of penetration into the stratum corneum was evaluated qualitatively by electron microscopy. Dermal penetration was also quantified using a tape stripping technique. Observations were compared with dermal penetration of the same materials applied as conventional scale particles.

SESSION AA2: Synthesis I
Chairs: Randy Simpson and William Wilson
Monday Afternoon, December 1, 2003
Liberty A-B (Sheraton)

1:30 PM *AA2.1
Synthesis and Characterization of Nanocrystalline Oxidizer/Monopropellant Formulations. Tom Brill, Bryce Tappan and Jun Li; university of Delaware, Newark, Delaware.

It is well known that the micro structural properties of energetic materials strongly influence the combustion and explosion behavior of the formulation. These differences can in part be attributed to the influence that the heat and mass transport rates have relative to the chemical kinetic rate on the overall heat generation rate. Making nano dimensional energetic materials is one strategy to enhance the role of chemical kinetics. Sol-gel methods of synthesis are well known in nano chemistry. We have added a different strategy to the sol-gel method by adding lyophilization in order to increase the amount to solid loading. Nano crystalline material loadings up to 90-95% of the composition by weight have been achieved. Hydrazinium diperchlorate and CL-20 have been incorporated into resorcinol-formaldehyde, nitrocellulose and glycidyl azide polymer gel matrices. Characterization was accomplished by SEM, TEM, AFM, DSC, T-jump/FTIR, drop hammer impact testing and visual observation of the combustion. The results were compared with those of physical mixtures having the same composition but with micron sized particles and found to be quite different. The use of non-metal nano crystalline materials in binder matrices appears to hold promise as a strategy to tailor the sensitivity and performance behavior of formulation

2:00 PM *AA2.2
Nanostructured Energetic Materials with Sol-gel Methods. Alexander E. Gash, Joe H. Satcher, Randall L. Simpson and Brady J. Clapsaddle; Energetic Materials Center, Lawrence Livermore National Laboratory, Livermore, California.

The utilization of nanomaterials in energetic and reactive material applications has launched alternative ideas on a previously mature field of investigation. This has lead to new concepts for the use of pyrotechnics, propellants, and explosives. Entirely new ways of storing and manipulating chemical energy are now being realized for a host of relevant applications. Elementary studies into the synthesis, characterization, modeling, safety, and energy release properties of these materials are currently being pursued at institutions worldwide and are critical to progress in this area. We have been investigating the use of sol-gel chemistry as a practical and safe approach to the synthesis and processing of energetic nanomaterials. The sol-gel method provides a straightforward and time-tested method for controlling particle size, particle morphology, porosity, purity, and composition of nanomaterials. In addition it is a versatile processing medium that can be used to prepare powders, monoliths, films, or even sintered bodies. Using methods advanced at LLNL a wide variety of sol-gel-derived nanometric oxidizers (e.g., Fe2O3 , WO3, NiO, MnO2) and a more limited set of nanometric fuels (e.g., hydrocarbon and carbon) have been prepared and characterized. The sol-gel method is also amenable to the preparation of intimately mixed nanocomposites. Several different thermitic and gas-generating energetic nanocomposite formulations have been prepared and their distinctive properties characterized. Results and details from synthesis, characterization, small-scale safety tests, and energy release studies will be presented.

2:30 PM *AA2.3
Formation of Nanostructured Energetic Materials via Modified Sol-Gel Synthesis. Rina Tannenbaum, Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Nanoenergetic materials are comprised of metal oxide nanoparticles closely mixed with metal fuel (e.g. Al, Fe, Cr). A stress-induced oxidation-reduction reaction results in a substantial exothermic heat release. The metal oxide is produced via sol-gel synthesis to form a porous wet oxide gel with a matrix consisting of 5-10 nm clusters. The fuel is subsequently introduced into the gel prior to solvent removal. The oxidant and fuel nanoparticles have a large contact area that ensures intimate mixing, hence increasing the energetic efficiency of the system. The heat released in these reactions and the gelation time have been controlled by varying reactants and solvents. In our preliminary studies, iron oxide gels were formed from hydrated iron salts, using both propylene oxide and some of its derivatives, and di-functional molecules (e.g. dicarboxylic acid) as the gelation agents, in an attempt to allow for the control of gelation kinetics and microstructure. Methanol, ethanol, butanol, hexanol, and octanol and mixtures thereof, were studied to evaluate the time to gelation as a function of solvent molecular size, boiling point and polarity. The results indicated that there is a direct correlation between the polarity of the solvent and the stabilization of the active gelation molecules. Additional experiments were conducted to probe the evolution of the reactive organic species during the gelation process, and determine the mechanism and kinetics of the reaction. This was achieved by modifying the pH of the original reaction solution through the addition of either dilute HCl or dilute NaOH. It is expected that the active gelation agent in the case of the epoxy-based materials or the di-functional molecules will be formed by different mechanisms, and hence, the acidity or the basicity of the original solution will have a different impact on the gelation process with either gelation precursors. The fuel used in these metal oxide xerogel systems were aluminum particles of two different types: micron-size and nano-size. It is expected that the intimate contact possible between nano-size aluminum particles and the nanoscale metal oxide xerogel network will provide a superior avenue for the optimization of the energy released upon application of stress, thus allowing the design of a highly efficient nanoenergetic materials system.

3:30 PM *AA2.4
Reactive Metal Composites: Energetic "Materials by Design". Jason Jouet and Andrea D Warren; Research and Technology Department, Naval Surface Warfare Center - Indian Head Div., Indian Head, Maryland.

The Navy has a need for reactive structural materials that can contribute to damage. These types of materials have application as reactive fragments, reactive ordinance cases, and reactive high velocity projectiles, to name a few. The specifications for such materials are extreme in that they must be able to survive high velocity and rapid acceleration yet react to impart damage upon impact to target. By chemically bonding metal particles together in a network type of arrangement the potential for extremely robust materials exists. By using Self-Assembly techniques, in which a chemical interaction takes place between a metal or metal oxide surface and a molecular species, we can efficiently "coat" the surface of metal particles. We can exploit this chemistry to functionalize the surface of both unpassivated nanoscale aluminum (nanoAl) and oxygen passivated aluminum (Op-Al) using carboxylic acids as coating agents. Further, by using difunctional acids, linear molecules with acid functionalities on both ends, we can "connect" the surfaces of two particles. By extrapolation we can create network solids of (different) metal and metal oxide particles with chemical linkage. In this way we begin to design new materials. Incorporation of various functional groups, such as F, NO_2, double and triple bonds, etc., in the molecular linkers, will allow for the potential for modifying the composite materials so that they can be tailored for the applications for which they are intended. Enormous potential exists for designing structural materials that incorporate various chemistries that when combined with the appropriate metals can survive launch, flight, and contribute to target damage as well as numerous applications yet to be envisioned. Passivation, coating, and networking experiments using

unpassivated and oxide passivated metals with various SAMs will be discussed. Characterization data including SEM, TEM, TGA, and IR of prepared materials will be presented.

4:00 PM AA2.5
On the Dispersion and Coating of Ultrafine Aluminum Powders by the Ziegler Natta Reaction. A Route to Form Metallic Powder/Thermoplastic Nanocomposites. Cedric Roy[1], Charles Dubois[1], Pierre Lafleur[1] and Patrick Brousseau[2]; [1]Chemical Engineering Department, Ecole Polytechnique, Montreal, Quebec, Canada; [2]Explosives and Propellants Group, Defence Research and Development, Valcartier, Quebec, Canada.

4:15 PM AA2.6
Preparation of Energetic Metastable Nano-Composite Materials by Arrested Reactive Milling. mirko schoenitz and Ed Dreizin; Mechanical Engineering, NJIT, Newark, New Jersey.

Highly metastable, nano-scale energetic materials were prepared by Arrested Reactive Milling (ARM). Reactive milling has been used previously to prepare stable and metastable alloys/intermetallic compounds by powder processing. In systems suitable for Self-Propagating High Temperature Synthesis (SHS), reaction between the components occurs spontaneously and violently after a certain period of milling. In this research, it was found that highly metastable nanocomposites could be prepared when the milling process was halted prior to the spontaneous transformation. Products thus obtained are intimate mixtures of reactive components, comparable to Metastable Intermolecular Composites (MIC), with near theoretical density. The time of arrest determines the degree of grain refinement and therefore the sensitivity to mechanical, electrical, or thermal initiation. While components are mixed on a nanometer to atomic scale, particle sizes of the product powders are in the micrometer range, and can be adjusted by appropriate choice of milling parameters. This paper describes the application of arrested reactive milling to the material systems including B-Ti and Al-MoO_3. After empirical determination of optimum milling parameters, the reactive composites are structurally characterized by electron microscopy and diffraction techniques. Reactivity is investigated in ignition and combustion tests and by thermal analysis. Preliminary aerosol explosion tests showed that ignition and combustion in air of nanocomposites of BTi and B_2Ti composition was greatly promoted by the nearly adiabatic boride formation reactions. The same tests for blends of elemental boron and titanium powders required higher igniter energies, while preformed borides could not be ignited at all. Combustion was incomplete for elemental blends; products showed both, residual boron and titanium, and borides. During combustion of the nanocomposites, particle temperature rose high enough to completely oxidize the material, no residual borides were detected in the combustion products.

4:30 PM AA2.7
Synthesis and Characterization of Mixed Metal Oxide Nanocomposite Energetic Materials. Brady J. Clapsaddle[1], Lihua Zhao[2], Alex E. Gash[1], Michelle L. Pantoya[3], Kenneth J. Shea[2], Joe H. Satcher[1] and Randall L. Simpson[1]; [1]Chemistry and Materials Science Directorate and Energetic Materials Center, Lawrence Livermore National Laboratory, Livermore, California; [2]Department of Chemistry, University of California, Irvine, Irvine, California; [3]Department of Mechanical Engineering, Texas Tech University, Lubbock, Texas.

In the field of composite energetic materials, properties such as ingredient distribution, particle size, and morphology, affect both sensitivity and performance. Since the reaction kinetics of composite energetic materials are typically controlled by the mass transport rates between reactants, one would anticipate new and potentially exceptional performance from energetic nanocomposites. We have developed a new method of making nanostructured energetic materials, specifically explosives, propellants, and pyrotechnics, using sol-gel chemistry. A novel sol-gel approach has proven successful in preparing metal oxide/silicon oxide nanocomposites in which the metal oxide is the major component. Two of the metal oxides are tungsten trioxide and iron(III) oxide, both of which are of interest in the field of energetic materials. Furthermore, due to the large availability of organically functionalized silanes, the silicon oxide phase can be used as a unique way of introducing organic additives into the bulk metal oxide materials. As a result, the desired organic functionality is well dispersed throughout the composite material on the nanoscale. By introducing a fuel metal into the metal oxide/silicon oxide matrix, energetic materials based on thermite reactions can be fabricated. The resulting nanoscale distribution of all the ingredients displays energetic properties not seen in its microscale counterparts due to the expected increase of mass transport rates between the reactants. The synthesis and characterization of these metal oxide/silicon oxide nanocomposites and their performance as energetic materials will be discussed. This Work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

4:45 PM AA2.8
Synthesis of Aluminum and Boron Nanoclusters By Inverse Micelle and Thermal Decomposition Methods.
Jess Patrick Wilcoxon, Stephen Woessner and Alex Tappan; 1122, Sandia National Laboratories, Albuquerque, New Mexico.

The rate of reaction of a pyrotechnic is limited by the diffusion of reacting oxidizer and fuel particles. This diffusion time is affected by the state of dispersion of the particles. Thus, methods to reduce particle size and increase interfacial area is a major goal in energetic materials (EM) research. We have developed two new wet chemical approaches to achieving small particle size and full dispersion of nanoparticles of Al and B. The first is by room T chemical reduction of suitable ionic aluminum precursors in the interior of inverse micelles. These micelles are water and air-free droplets which form spontaneously in oil/surfactant solutions and are capable of solubilizing ionic species. Dispersed clusters in the size range from 1.6 to 4 nm may be made by this method and importantly, these particles have no oxide on their surface. Alternatively, we thermally decompose organo-aluminum precursors at modest temperatures around 100 C in the presence of various amounts of surfactants to control the final cluster size. In both cases the reactions take place in an inert Ar atmosphere. The nanoclusters produced by either process can serve as seed nanocrystals onto which Cu, Fe, or W may be deposited, followed by oxidation to passivate the surface and allow easier processing. Dynamic light scattering and liquid chromatography are used to characterize the nanoparticles. Acknowledgement: This work was supported by the Sandia Laboratory Directed Research and Development program; the Defense Threat Reduction Agency; and the Division of Materials Sciences, Office of Basic Energy Research, US Department of Energy under contract DE-AC04-94AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

SESSION AA3: Poster Session
Chairs: Zuhair Munir and Naresh Thadhani
Monday Evening, December 1, 2003
8:00 PM
Exhibition Hall D (Hynes)

AA3.1
Influence of Catalysts on the Morphologies of Multiwalled Carbon Nanotubes Prepared by Carbon Arc Cathode Deposit. Weizhong Zhu, D. E. Miser, W. G. Chan and M. R. Hajaligol; Philip Morris USA, Richmond, Virginia.

Multiwalled carbon nanotubes prepared by carbon arc cathode deposit using various catalysts were characterized by scanning electron microscopy, high resolution transimission electron microscopy, X-ray diffraction, and BET surface measurement. Experimental results indicate that besides carbon nanotubes, the deposit also contains amorphous carbon particles, multi-layered polygonal carbon particles, and large graphite platelets. Various tube motphologies are revealed by phase contrast HRTEM images, which are associated with different catalyst behaviors involved in the tube growth. Within reasonable fluctuation range, fast Fourier transform results and XRD profiles offer essentially identical structrual information. The deposit is found to exhibit a broad pore distribution, which is independent of catalyst used in the preparation.

AA3.2
A Hybrid Laser Vaporization - Hot Wire Chemical Vapor Deposition Synthesis of Single Wall Carbon Nanotubes.
Thomas Gennett[1], William R. VanderVeer[1], Ryne P. Raffaelle[1], Michael J. Heben[2], Kim M. Jones[2] and Anne C. Dillon[2]; [1]NanoPower Research Laboratory, Rochester Institute of Technology, Rochester, New York; [2]National Renewable Energy Laboratory, Golden, Colorado.

A hybrid laser vaporization-hot wire chemical vapor deposition synthesis has been demonstrated for the continuous generation of single-walled carbon nanotube (SWNT) materials. In this synthesis the carbon feedstock was generated by the laser vaporization of a pure graphite target with the resultant plume directed over a hot nickel filament in a static argon atmosphere. The SWNT materials that condensed in the chamber were collected and analyzed with Raman Spectroscopy and Transmission Electron Microscopy. The resultant soot contained a mixture of nanostructured graphite, SWNTs and trace amounts of metal catalyst. The tube diameters were a mixture of both semiconducting and metallic SWNTs ranging from 1.1 - 1.5

nm. The specifics of the system design and implications on the mechanism of nanotube growth will be presented.

AA3.3
Synthesis and characterization of metal alloy nanoparticles for advanced fuel cell catalysis. Peter N Njoki, Jin Luo, Li Han, Mathew M Maye and Chuan-Jian Zhong; Chemistry, SUNY-Binghamton, Binghamton, New York.

Nanostructured materials are showing great promises for energy storage and fuel cell catalysis. The challenge is to precisely control the size and composition of the nanostructures. This presentation discusses recent results of an investigation of the refinement of the synthetic and processing protocols for the control of size and shape of metal alloy and semiconductor nanoparticles. The work is aimed to understand the fundamental basis of the control parameters. The preparation of Au-containing alloy nanoparticles and GaAs nanoparticles is investigated. Transmission electron microscopy, infrared reflection spectroscopy and atomic force microscopy have been used to characterize the size, structural and morphological properties of the nanostructures. The alloy composition in the nanostructure determined by direct current plasma-atomic emission spectroscopy has been correlated with the synthetic feed composition. Implications of the results to the design of binary functional nanomaterials will also be discussed.WITHDRAWN - 10/06 - PER ON-LINE CONFIRMATION ABSTRACT RE-INSTATED 10/9 - PER AUTHOR, C.J.ZHONG

AA3.4
Correlation of Oxidation Steps and Phase Transformations In Al-Ti Mechanical Alloys. xiaoying zhu, mirko Schoenitz and Edward L Dreizin; Mechanical Engineering, New Jersey Institute of Technology, Newark, New Jersey.

Mechanical alloys (MA) in the Al-Ti binary system with compositions ranging from Al0.95Ti0.05 to Al0.7Ti0.3 were synthesized as potential fuels for high energy density materials. Preliminary experiments showed increased burn rates of mechanically alloyed powders compared to pure aluminum. Phase transformations occurring in MA have been studied using differential scanning calorimetry (DSC). This work is aimed at characterization of oxidation behavior of Al-Ti mechanical alloys using DSC and thermo-gravimetric analysis (TGA). Pure Al and Ti powders, MA powders, and Al/Ti powder blends with respective elemental compositions are heated at 15 K/min in oxygen up to 1500C. Oxidation steps observed in these experiments are identified, partially oxidized powders are quenched and their phase compositions are studied using x-ray diffraction. Differences in the oxidation steps for alloys and respective pure metal powder blends are specifically addressed. Also studied are correlations between the oxidation steps and phase transformations occurring in the same Al-Ti MA upon annealing in oxygen and inert environment, respectively. It is observed that alloys with lower Ti concentrations experience three sequential oxidation steps, around 730C, 950C, and 1370C. The first oxidation step correlates with the formation of stable Al3Ti phase occurring in both MA and pure metal powder blends upon annealing in argon. The second oxidation step appears to correlate with an endothermic phase transition found to occur only in Al-Ti metastable MA and resulting in the release of aluminum melt. The third oxidation step correlates with the liquidus in the equilibrium system. As the concentration of Ti in MA increases, the first oxidation step gradually disappears. Both second and third oxidation steps occur over increasingly broader temperature ranges. In addition, the onset of the third oxidation step shifts towards lower temperatures. Further analyses of the quenched samples and DSC/TGA data processing are expected to identify sequences of oxidation processes and specific reactions occurring in different material systems. This information will help modeling ignition of respective materials used as fuels or fuel additives in energetic materials.

AA3.5
Dependence of vertically aligned the growth of carbon nanotubes on the catalysts. Nam Seo Kim, Seung Yong Bae and Jeunghee Park; Chemistry, Korea University, Seoul, South Korea.

We report the catalytic effect on the synthesis of multiwalled carbon nanotubes (CNTs). The CNTs were grown vertically aligned on the iron (Fe), cobalt (Co), and nickel (Ni) catalytic nanoparticles deposited on alumina substrates by thermal chemical vapor depositon of acetylene in the temperature range 900-1000 °C. We also synthesized them on the silicon oxide substrates by pyrolyzing iron phthalocyanie (FePc), cobalt phthalocyanie (CoPc), and nickel phthalocyanine (NiPc) at 700-1000 °C. In both syntheses, the CNTs grown using Fe exhibit about 2 times higher growth rate than those using Co and Ni. As the temperature rises from 700 to 1000 °C, the growth rate of CNTs increases by a factor of 45. The Arrhenius plot of growth rates provides the activation energy 30±3 kcal/mol for all three catalysts, which is similar with the diffusion energy of carbon in bulk metal. It suggests that the bulk diffusion of carbon would play a decisive role in the growth of CNTs. The diameter of CNTs is in the range of 20-100 nm, showing an increase with the temperature. As the diameter is below 30 nm, the CNTs usually exhibit a cylindrical structure. The CNTs were intrinsically doped with the nitrogen content 2-6 atomic %. The degree of crystalline perfection of the graphitic sheets increases with the temperature, but depends on the catalyst and the nitrogen content. The graphitic sheets of CNTs grown using Fe are better crystalline than those grown using Co and Ni. As the nitrogen content increases, the degree of crystalline perfection decreases and the structure becomes the bamboo-like structure probably due to a release of strains.

AA3.6
Effect of Microwave Synthesis on the Structure of Carbon Nanotubes. Oxana Vasilievna Kharissova and Sergio Javier Mejia-Rosales; FCFM, UANL, San Nicolas de los Garza,, Nuevo Leon, Mexico.

Carbon nanotubes were synthesized from graphite using microwave (MW) heating (power 800 W, frequency 2.45 GHz) in vacuum (10-4 Torr) for 30-90 min. The morphology of the carbon nanotubes was studied by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and Transmission Electron Microscopy (TEM). Using the AFM, nanotubes were caught on a raw sample and then deposited on a clean surface with an absolute precision better than 500 nm. Measurements of distinct angles, distances, and spaces between waves were made. The measurements by AFM were then compared with the geometries of various models of multi-walled nanotubes (MWNTs).

AA3.7
Nanoindentation to Characterize Porous NiTi Produced via Combustion Synthesis. Reed Ayers[1], Virginia Ferguson[2], Denise Belk[1], Kenneth Gall[3] and John J. Moore[4]; [1]CCACS, Colorado School of Mines, Golden, Colorado; [2]BioServe Space Technologies, University of Colorado, Boulder, Colorado; [3]Department of Mechanical Engineering, University of Colorado, Boulder, Colorado; [4]Department of Metallurgical and Materials Sciences, Colorado School of Mines, Golden, Colorado.

Porous nickel-titanium (NiTi) produced via combustion synthesis (SHS) has pore sizes that range from microns to millimeters in size and is ideal for bone engineering applications. Nanoindentation, used to directly probe the elastic modulus and hardness of small volumes of material, overcomes the difficulties in mechanically testing this porous material that are encountered by larger scale techniques. We used nanoindentation to measure site-specific material properties of porous NiTi produced via SHS. Indent arrays (5x5 indents; 1750nm max depth) + 10 marker indents (2500nm): Berkovich indenter tip) were positioned in a uniformly polished, optically flat region of single crystal NiTi. Two indent arrays (10x10 indents; 750nm and 1500nm max depth to account for a possibility of a martensitic/austenitic phase change noted in previous studies) were located in uniform regions of polished porous SHS NiTi using a MTS Nanoindenter XP (MTS, Eden Prarie, MN). In SHS materials, indentations landing on or intersecting pores or a thin layer of intermetallics (NiTi2, Ni3Ti4, etc.) were discarded. Material surfaces were characterized using x-ray diffraction, and SEM/EDS was used to examine material stoichiometry within the indent arrays. Hardness and indentation modulus of the porous SHS NiTi was consistent with values obtained from single crystal NiTi (76.9±1.4 and 5.4±0.3 GPa, respectively), and did not vary with maximum indenter contact depth of 750nm (88.8±8.2 and 6.2±0.6 GPa) or 1500nm (87.8±8.2 and 5.7±0.6 GPa). The single crystal composition was Ti - 50.5 at% Ni, compared to the SHS porous NiTi of Ti - 50.2 at% Ni and Ti - 50.7 at% Ni in regions testing at 750nm and 1500nm depths, respectively. Large variance in SHS NiTi modulus and hardness likely resulted from the presence of other intermetallics but was not influenced by porosity. Nanoindentation was able to directly measure the material properties of the SHS NiTi without being affected by porosity.

AA3.8
Preparation and Characterization of Nano-Sized Orthorhombic Lithium Manganese Oxide Powders. Chung-Hsin Lu[1], Hsien-Cheng Wang[1] and Yu-Kai Lin[1]; [1]Chem. Eng., National Taiwan Univ., Taipei, Taiwan; [2]National Taiwan Univ., Taipei, Taiwan.

Lithium-ion secondary batteries are important power sources for portable electronics, such as laptop computers, cellular phones, and camcorders. In addition, they are also considered as the promising candidates for use in the electric vehicles. In the Li-Mn-O system, orthorhombic $LiMnO_2$ (o-$LiMnO_2$) with an ordered-rocksalt structure has been considered a promising cathode material in lithium-ion rechargeable batteries. In this study, nanosized orthorhombic $LiMnO_2$ were successfully synthesized using a newly developed

reverse-microemulsion (RμE) process. To prepare o-$LiMnO_2$ powders with a rock salt structure, precise control of the oxygen content in the heating atmosphere was required. Monophasic o-$LiMnO_2$ was obtained at as low as 700°C. The reaction temperature was lowered and the reaction duration for synthesizing the desired powders was also markedly shortened via the RμE route. The discharge capacities of the prepared o-$LiMnO_2$ powders significantly increased in the initial stages, and rapidly reached a saturated plateau. The impedance spectroscopy analysis revealed that the chemical diffusion coefficient of lithium ions in o-$LiMnO_2$ was markedly greater than that in $LiMn_2O_4$-based materials.

AA3.9
Dislocation Structure of The HAZ Formed During Spot Welding of Ni-Based Single Crystals. Oleg M Barabash, Stan A David, John M Vitek, Jin W Park, Joe A Horton, Suresh S Babu and Rozaliya I Barabash; Metals and Ceramics Div., Oak Ridge National Laboratory, Oak Ridge TN, Tennessee.

Nanosize Ni3Al particles are responsible for strengthening of the TSM75 Ni based superalloy. Their volume fraction reaches 65%. A heat affected zone (HAZ) was formed during local melting and solidification of the end of a cylindrical sample (diameter of the rod is 13mm and length 60 mm) of TSM75 Ni-based single crystal. Thermal gradients during local melting and solidification of the end of the sample were simulated by taking into account heat conduction. Heat loss on the surface by convection and radiation was also considered in the simulation. We found that he change in temperature gradient is maximal in the HAZ close to solidification front. Varying thermal gradients produced under such conditions may cause stresses and plastic deformations. The dislocation structure in the HAZ was studied by X-ray Laue diffraction. It was established that after cooling the dislocation density is minimal in the melted zone. Approaching the fusion line the dislocation density sharply increases and reaches a maximal value in the HAZ at the distance coinciding with the position of the maximal change of temperature gradient. There after, the dislocation density slowly decreases and reaches a minimal value outside the HAZ. Analysis of Laue images indicated the formation of unpaired edge dislocations with Burgers vector and dislocation lines along the directions <101>, [1-21] and <1-10>, [1-21]. Within the analyzed regions of r 0.5mm, these unpaired dislocations cause local rotation around the axes [010] in the plane (00-1).

SESSION AA4: Synthesis II
Chairs: Dana Dlott and Bob Wardle
Tuesday Morning, December 2, 2003
Liberty A-B (Sheraton)

8:30 AM *AA4.1
Combustion Synthesis of Nanomaterials: Mechanism, Characterization and Properties. Arvind Varma, Alexander S Mukasyan, Kishori T Deshpande, Pavol Pranda and Peter R Erri; Chemical & Biomolecular Eng, University of Notre Dame, Notre Dame, Indiana.

An approach related to the sol-gel route, where an aqueous solution of suitable oxides or salts is mixed with an alpha-hydroxycarboxylic acid, is known as the Pechini, or liquid mix, process. Similarly, combustion synthesis (CS) is an energy-efficient method to synthesize a large variety of solid-state materials and is characterized by fast heating rates, high reaction temperatures and short reaction times. A combination of these two approaches leads to the so-called $aqueous (or solution) combustion synthesis$. One version of this process involves a $self-sustained$ reaction in solution of metal nitrates and different fuels, which can be classified based on the type of reactive group bonded to the carbon chain. These fuels provide high temperature rapid interaction in the system, reacting with oxygen containing species formed during the nitrates decomposition. More specifically, after preheating to moderate temperatures ($\sim 150^o$ -200^o C), the reaction medium ignites and reaction front propagates along the system, leaving behind solid product of tailored composition. The following features of aqueous CS contribute towards the unique material properties obtained. First, using water solutions of the precursors allows mixing the reactants on the $molecular$ level that permits precise and uniform formulation of the desired product composition. Second, the powder synthesis typically occurs at high temperatures ($\sim$ 800°C) for very short period ($\sim$1 s), resulting in $high purity$ and $crystallinity$. These features allow one to skip the intermediate calcination step typically followed in conventional approaches. Third, during the rapid exothermic reaction, many gases (from both oxidizer and fuel) are released, inhibiting particle size growth and thus promoting formation of nano-powders with high specific surface area (in the range 30-180 m^2/g). Different types of oxide nanopowders were synthesized in our laboratory using this approach, including binary iron oxides (α- and γ- Fe_2O_3 and Fe_3O_4 phases) and complex lanthanide-based perovskites, useful for magnetic, catalysis and fuel cell applications. More importantly, based on the analysis of extensive experimental data, we have formulated basic criteria necessary to perform synthesis in the combustion mode, and defined parameters to optimize synthesis conditions for production of high-surface area, well-crystalline nano-powders of desired phase composition and purity. Also, for the first time, detailed chemical mechanisms of interaction in the combustion wave for various systems (e.g. Fe-based, Co-based and Ni-based) were formulated, outlining specific roles of different fuels and thermal conditions. The results presented in this work demonstrate clearly that the aqueous CS approach, involving rapid high temperature reaction in solutions of organic and inorganic precursors, is a powerful tool for the synthesis of a variety of valuable nano-materials.

9:00 AM *AA4.2
Mechanical Alloying and Burning of Al-Mg Particles. C. Suryanarayana, Devender Singh and Ruey-Hung Chen; Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, Florida.

To enhance the performance of rockets, it is desirable to have as high as possible an energy density of the propellants. It is known that some metals contain higher energy densities than commonly used chemical propellant. However, they can be more difficult to ignite and burn. One such metal propellant is aluminum (Al). To facilitate its burning, magnesium (Mg), which has a much lower ignition temperature than Al, can be added. However, it is not known how much improvement can be achieved, or how Mg and Al should be mixed for such purposes. In this experimental program, a materials processing technique called mechanical alloying is used to make Al-Mg alloy particles. X-ray diffraction was used to examine the alloy particle before and after burning to extract the information regarding how complete the burning is and how much energy in the metal propellant is realized. The alloy particles can be made and sifted to narrow size ranges (20 to 90 mm) for better quantification of the burning process. The ignition and burning was recorded in movies and in both direct and chopped still photograph modes. The chopped images make possible detail analyses of ignition and burning times. Initial results will be presented, along with data available in the existing literature. Work in progress and for the future will also be discussed.

9:30 AM *AA4.3
Kinetics & Energetics of Nano Energetic Materials. Mana Pai, Conducting Materials Corp., Columbia, Maryland.

The role of nano aluminum in performance enhancement of energetic materials, specially, solid composite propellants is well known. The beneficiary is the burn rate. Combustion itself can be transformed into explosion. However, the effect on energy output and the safety parameters have not been addressed adequately. Unpassivated nano Al can find a place in hybrid combustion without energy loss associated with passivation. We will discuss this aspect. We will also discuss briefly data on laser initiation of surface tension energy and thermite reaction. The advantages of nanoporous energetic materials over nano energetic materials will be highlighted. Typically, nickel aluminide formation by solid state reaction at low temperatures (100°C) will be illustrated.

10:30 AM *AA4.4
High-Pressure High-Temperature Sintering of Reactive Nanomaterials. Suhithi M Peiris, Research and Technology Department, Naval Surface Warfare Center - Indian Head, Indian Head, Maryland.

The objective of our work is to sinter nano materials to yield nano-structured materials that are more robust than the nano material and still retains the reactivity of the nano material. We use diamond anvil cells with heating coils to sinter or press and heat micro-quantities of nano materials. The heating temperature and pressure are chosen after investigation of the structural changes of the nano material with pressure and temperature. We investigate structural changes and melting temperatures using DTA, x-ray diffraction, and SEM, and measure hardness using Vicker's Hardness testing. Preliminary work on 152nm nano Aluminum indicated that first heating and then pressing yields harder materials. Further, sintering nano Al did result in a material with higher hardness than bulk Al. This work on nano Al, and other nano materials will be presented.

11:00 AM *AA4.5
Combustion Synthesis of NiTi-TiC Composites with Controlled Porosity for Biomedical Applications. Douglas E. Burkes[1,2], Guglielmo Gottoli[1,2], Reed A Ayers[2] and John J. Moore[1]; [1]Metallurgical and Materials Engineering, Colorado School of Mines, Golden, Colorado; [2]Center for Commercial Applications of Combustion in Space (CCACS), Colorado School of Mines, Golden, Colorado.

Combustion synthesis, or Self-propagating High-temperature Synthesis (SHS), is currently being used by the Center for Commercial Applications of Combustion in Space (CCACS) at the Colorado School of Mines to produce advanced porous materials for several important applications. These materials include ceramic, inter-metallic, and metal-matrix composites that can be used for orthopedic implants, heat exchanger and damping systems and micro-and macro-filter applications. Functionally graded materials, both in porosity and composition, can be produced using a range of combustion synthesis reactions systems. There are multiple factors that contribute to the final SHS product, e.g. reactant stoichiometry, green density and pre-heat. The synthesis of nickel-titanium (NiTi) intermetallic compounds and composites is of considerable interest due to the ability to create a porous, shape memory and super-elastic alloy with high corrosion resistance. The synthesis effects of adding a carbon reactant so as to modify the reaction products and reaction exothermicity have been studied through the use of three different reaction stoichiometries involving elemental nickel, titanium and carbon. The paper outlines the synthesis of NiTi intermetallic compounds and composites based on the following SHS reaction: xNi + (x + y)Ti + yC = xNiTi + yTiC. In addition, the effect of the carbon reactant and the initial sample green density on the general apparent porosity of the final materials has been studied and is presented within this paper. A NiTi-TiC intermetallic ceramic composite has been synthesized that is functionally graded in both composition and porosity due to buoyancy and capillary effects. The kinetic mechanisms that drive this synthesis process and control the graded structure are discussed in detail.

11:30 AM AA4.6
Combustion Synthesis of Nanocomposite Al/Ni.
Emily McFather Hunt and Michelle L Pantoya; Mechanical Engineering, Texas Tech University, Lubbock, Texas.

In the combustion synthesis of metal alloys, metallic reactants are ignited and self-propagating heat waves create new materials at heating rates up to 104 to 10$\hat{6}$ K/s. Nano-scale reactant particles offer increased homogeneity in the reactant mixtures and potentially improved micro-structural features of the products. However, nano-aluminum is pyrophoric and thus each particle is coated with an alumina passivation layer. Because the surface area to volume ratio increases dramatically for nano-scale particles, this passivation layer can result in 50% of the total Al powder. Therefore, the effect of increasing mass percentage of alumnina on the combustion and product formation of Al/Ni is a focus of this study. Pressed pellets were ignited at one end, and flame propagation and temperature measurements were made using high-speed diagnostics and micro-thermocouples. Another objective is to increase the heating rate and improve microstructural properties by adding nano-particle solid oxidizers. For example, molybdenum trioxide (MoO3) and Al generate a highly exothermic reaction. Small quantities of MoO3 were added to the Al/Ni composite to examine the effect of heating rate on combustion behavior and product formation. Electron micrographs of the products were taken to compare the final microstructure of the new alloy to the nickel almnide composite. Results from these experiments indicate that the burn velocity of the nickel alumnide system is increased by the addition of the nano-scale MoO3 to the initial reactants. Spectroscopy was also used to determine the temperature of the combustion front in both systems, and the new alloy exhibited a higher combustion temperature and increased heating rates. Thus, a new material is formed with faster burn rates and higher temperatures, which may prove to increase the overall strength and structure of the product.

11:45 AM AA4.7
Interface and Surface Properties of Al/Ni Multilayers as Deposited and Following Volume Combustion Synthesis.
Mark Holtz, D. Aurongzeb, M. Daugherty, A. Chandolu, J. Yun, J. Berg and H. Temkin; Texas Tech University, Lubbock, Texas.

We report a volume combustion synthesis study of Al/Ni multilayers. The alternating layers of pure Al and pure Ni were grown on silicon and glass substrates using electron beam evaporation. Layers of equal thickness and with bilayer period of 50 nm were grown with total thickness to 1 micron. Growth is terminated with a Ni layer to minimize complications associated with Al oxidation. We focus in this study on the interface properties of as deposited multilayers and following anneals up to 760 C with 100 C intervals. Anneal duration was generally 10 min; longer anneals were performed to verify consistency with previously published results. Interface structure was probed using X-ray reflectivity (XRR). Analysis of the XRR provides interface roughness values of the as-deposited layer of 2 nm, in good agreement with the substrate surface roughness. The period obtained from the XRR is between 48 and 54 nm for all cases where interference fringes are observed. This value is in good agreement with the 50 nm period from deposition and the 52 nm period from SEM cross-sections. We identify four temperature ranges. In the as-deposited to 260 C anneal range the interface properties remain intact, as seen from the XRR interference fringes beyond the critical angle. From anneal temperatures 360 to 460 C fringes disappear, indicating the loss of smooth interface morphology. We describe this using a model in which alloy domains form at the interface and grow with temperature and time. SEM cross-sections confirm this picture. The third anneal temperature range is 500 to 560 C. In this temperature range the XRR interference fringes are clearly seen, signifying the presence of layering with the same periodicity of the as-deposited layers. We interpret this using the above model incorporating the difference in lateral and vertical growth rates of alloy domains. At 660 C, the melting temperature of Al, and above the fringes completely vanish. X-ray diffraction is used to identify the nickel aluminide compounds formed upon anneal. Atomic force microscopy and plan-view SEM reveal surface roughness. At 360 C and above, we observe the formation of hillocks. This work is supported by the National Science Foundation under grant CTS 6086406.

SESSION AA5: Characterization
Chairs: John J. Gilman and Tom Russell
Tuesday Afternoon, December 2, 2003
Liberty A-B (Sheraton)

1:30 PM *AA5.1
Ultrafast spectroscopy of laser-initiated nanoenergetic materials. Dana D. Dlott, Yanqiang Yang, Zhaoyong Sun and Wang Shufeng; School of Chemical Sciences, University of Illinois, Urbana, Illinois.

A picosecond laser flash-heating technique is used to initiate chemistry in nanoenergetic materials consisting of Al or B nanoparticles with a variety of oxidizers. The time dependence of chemistry is probed using ultrafast Raman, IR and emission spectroscopy. The spatial dependence of chemistry is probed by combining the time-resolved results with concentration-dependent measurements where the distance between nanoparticles is varied.

2:00 PM *AA5.2
Performance and Characterization of Nanoenergetic Materials at Los Alamos. Steven F. Son, LANL, Los Alamos, New Mexico.

Novel properties associated with nanostructured materials, including nanoenergetic 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 combustion velocities above 1 km/s. These properties make them very attractive in a number of applications, including lead-free primers and igniters. However the mechanism responsible for the propagation of reaction in loose compacts is not well understood. Of the four possible candidates (radiation, convection, conduction, and acoustic/compaction), these preliminary studies identify convection as the most likely. In this paper we will present an overview of efforts at Los Alamos to understand the reaction mechanisms of these advanced energetic materials. We will also review our efforts to characterize these materials.

2:30 PM *AA5.3
Ignition and Combustion Behaviors of Nanocomposite Thermites. Michelle Pantoya, Mechanical Engineering Department, Texas Tech University, Lubbock, Texas.

Recent advances in the field of nanotechnology have focused attention on developing nanocomposite thermites with enhanced energy release rates and increased sensitivity to ignition. Characterization of nano-particles is also important for explaining unique combustion behaviors of micron vs nano-composites. To this end, a new technique for analyzing particle size distributions will be discussed using DSC. Particle size distributions were performed on nano-scale Al particles. This technique makes use of the variation in melting temperature with Al particle size. This study also compares the combustion behavior of Al and Fe2O3 composites synthesized from nano-scale reactant powders versus synthesized using sol-gel processing. Three nano-scale Fe2O3 oxidizers were compared including an aerogel, xerogel and commercially obtained Fe2O3. Burn rates were measured by igniting the mixture at one end and using ultra-high speed imaging diagnostics. Ignition time, temperature and energy were examined using a CO2 laser ignition apparatus and micro-thermocouples. Open and confined burning of powder material was examined. Confined burns were performed in Acrylic tubes that ranged in diameter from 0.25 to 0.125 inch diameter. Additional ignition tests were performed on pressed pellets. For the powder composites the effect of Al particle size was evaluated by varying the Al particle size from 17 nm to 1

micron in diameter. Initial studies indicate that these materials propagate at very high rates (>500 m/s). Many factors influence burning rate. For example, bulk density and stoichiometry play an integral role in determining burn rate. Results show an increase in ignition sensitivity with decreasing Al particle size. The oxidizer synthesis technique was also shown to influence the burn rate measurements. Information on issues such as reaction rate, ignition energy, and combustion behavior as a function of density, composition and particle size are essential and will allow scientists to design applications incorporating the benefits of these compounds. Results from this research could have an impact on the handling and use of energetic materials.

3:30 PM *AA5.4
The Shock Initiation And High Strain Rate Mechanical Characterization Of Ultrafine Energetic Powders And Compositions. J. E. Field, W. G. Proud, M. W. Greenaway, C. R. Siviour, J. E. Balzer and S. M. Walley; Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom.

This review covers current areas of research on ultrafine energetic materials in our laboratory. The first topic concerns laser flyer initiation using flyers of micron-thickness travelling at a few km s^{-1} [1]. It was found first that powders with conventional sized grains (0.1-1mm size) were insensitive to laser flyer shocks as the shock thickness produced is much smaller than either the grains or the pore spaces between them. However, prompt initiation of ultrafine materials is possible [2]. The density of the ultrafine powders was found to have a strong effect on the laser energy needed to produce detonation and this has been quantified [3]. The high rate mechanical strength of AP/HTPB compositions with four different particle sizes ranging from 3-300 microns has been investigated using a compression split Hopkinson pressure bar [4]. It was found that the sensitivity of high rate flow stress to particle size was most pronounced at low temperature (-60°C) and followed an inverse square root relationship [5]. Conventional and ultrafine material has also been subjected to drop-weight impact using our transparent anvil systems combined with high-speed photography [6]. This allows us to identify the mechanisms of ignition for the various materials. Finally, a sensitive gap test has been developed and data on ultrafine materials will be presented. References 1. Greenaway, M.W., "The development and characterisation of a laser-driven flyer system", PhD thesis, Univ. of Cambridge, (2001) 2. Chakravarty, A., Gifford, M.J., Greenaway, M.W., Proud, W.G., and Field, J.E., "Factors affecting shock sensitivity of energetic materials", in "Shock Compression of Condensed Matter - 2001", ed. M.D. Furnish, N.N. Thadhani, and Y. Horie, pp. 1007-1010, publ. American Institute of Physics, Melville, NY, (2002) 3. Greenaway, M.W., Gifford, M.J., Proud, W.G., Field, J.E., and Goveas, S.G., "An investigation into the initiation of hexanitrostilbene by laser-driven flyer plates", in "Shock Compression of Condensed Matter - 2001", ed. M.D. Furnish, N.N. Thadhani, and Y. Horie, pp. 1035-1038, publ. American Institute of Physics, Melville, NY, (2002) 4. Siviour, C.R., Walley, S.M., Proud, W.G., and Field, J.E., "Hopkinson bar studies on polymer bonded explosives", in "Proc. 6th Seminar on New Trends in Research of Energetic Materials", ed. J. Vágenknecht, pp. 338-349, publ. University of Pardubice, Pardubice, Czech Republic, (2003) 5. Balzer, J.E., Siviour, C.R., Walley, S.M., Proud, W.G., and Field, J.E., "Behaviour of ammonium perchlorate-based propellants and a polymer-bonded explosive under impact loading" *Proc.R.Soc.Lond.* A (2003) (accepted for publication) 6. Balzer, J.E., Field, J.E., Gifford, M.J., Proud, W.G., and Walley, S.M., "High-speed photographic study of the drop-weight impact response of ultrafine and conventional PETN and RDX" *Combust.Flame* **130** (2002) 298-306

4:00 PM *AA5.5
Preparation and Characterization of Nanoenergetic Materials for Explosive Applications. Michael P. Kramer, AFRL/MNME, Eglin AFB, Florida.

Historically aluminum has been added to explosive formulations to enhance blast performance. However, the expected energy contribution associated with the combustion of aluminum has not been achieved due to the incomplete combustion of aluminum and the accompanying slow burn rate associated with micron-sized material. Recent efforts using nanometric aluminum in propellants has demonstrated that the addition of nano-sized particles increases burn rates and improves the efficiency of the combustion reaction of aluminum. This increase in performance can be directly attributed to the large surface area per unit volume of the nano-sized particle, their accompanying high surface free energy, and the reduce reaction coordinate. The direct substitution of nano-sized aluminum for micron sized aluminum in propellant and explosive formulations is difficult due to the rheology problems associated with the addition of small particle, high surface area materials. Small particle size materials are more difficult to wet and disperse effectively at the solids loadings typical for current propellant and explosive formulations. These poor flow properties lead to poor quality formulations that do not meet performance expectations. Additional problems associated with reducing the particle size of aluminum is the active aluminum content on a mass basis. The typical passivated aluminum particle has an oxide coating of approximately 4 nanometer thickness which for a micron sized aluminum particle on makes up about 1 to 3 percent of the mass. However, at the 30 nanometer size, that same 4 nanometer thick oxide shell now constitutes 40 plus percent of the total mass of the particle. This loss of active aluminum and the accompanying rheology problems has to our novel approach to utilizing nano-aluminum. In an attempt to over come the rheology difficulties inherent with processing nano-sized aluminum, a study was undertaken to coat the small particle size, high surface area aluminum with an organic explosive molecule. The coating technique allows for an intimate mixing of the explosive crystals and the aluminum, and a homogeneous dispersion of the aluminum throughout the formulation. The oxide coating present on the aluminum's surface is protected and the energy content is maintained. Initial safety and handling testing of the coated aluminum materials reveals a significant decrease in the sensitivity of the materials. These observations are not unexpected based on the intrinsic mechanical strength properties of nano-sized metals. This effect is additionally supported by the reduction in crystal size of the organic high explosive. Characterization of these materials using several complimentary analytical techniques are reported.

4:30 PM *AA5.6
Application And Characterization Of Nanomaterials In Energetic Compositions. Antoine E. D. M. van der Heijden, R. H. B. Bouma and A. C. van der Steen; Research Group Pyrotechnics and Energetic Materials, TNO Prins Maurits Laboratory, Rijswijk, Netherlands.

As part of a cooperation between several TNO institutes, including TNO Prins Maurits Laboratory, recently a new initiative on nanotechnology was started. The research subjects within this initiative can be roughly divided into two areas: (1) Instrumentation for analysis and manufacture at nano-scale and (2) Nanoscale engineering techniques to create materials and components (including their applications). Currently the research at TNO Prins Maurits Laboratory is focusing on the application of reactive nanomaterials to decontaminate surfaces from e.g. bacteria or toxic chemicals, the use of plasma's to generate nanomaterials like carbon nano-tubes, and the application and characterization of nanomaterials in energetic formulations (e.g. explosives, propellants and pyrotechnic compositions). In this paper results on the latter subject will be presented in more detail. Also results will be included of other research projects involved with energetic/reactive nanomaterials.

SESSION AA6: Characterization and Theory
Chairs: Michael Bermann and David M. Mann
Wednesday Morning, December 3, 2003
Liberty A-B (Sheraton)

8:30 AM *AA6.1
Ab-initio Calculation of the Equation of State for Organic Molecular Crystals. Frank J. Zerilli[1] and Maija M. Kuklja[2]; [1]Research and Technology Department, Naval Surface Warfare Center, Indian Head, Maryland; [2]Division of Materials Research, National Science Foundation, Arlington, Virginia.

In recent years, a large body of research has been devoted to the determination of the equation of state of many solids through numerical solutions of the many-body Schrödinger equation. Most of the work has concentrated on metals, elementary solids, metal oxides, and ionic solids. In this work, we describe the calculation of the 0 K isotherm for several organic molecular crystals, including 1,1-diamino-2,2-dinitroethylene and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane. With relaxation of both molecular geometry and lattice parameters under compression, standard Hartree-Fock solutions give results that compare well with experimental measurements. Density Functional Theory calculations give much poorer results. We also discuss the extension of these calculations to the full temperature dependent equation of state.

9:00 AM *AA6.2
Embedded Cluster Model: Application to Molecular Crystals. Maija M Kukla[1], Frank J Zerilli[2], Peter V Sushko[3] and Alexander L Shluger[3]; [1]Division of Materials Research, National Science Foundation, Arlington, Virginia; [2]Indian Head Division, Naval Surface Warfare Center, Indian Head, Maryland; [3]Physics and Astronomy, University College London, London, United Kingdom.

Multiscale modeling based on a hybrid quantum mechanics/classical mechanics method implementing an embedded cluster approach is presented and applied to studies of molecular crystals. We discuss

advantages and disadvantages of the embedded cluster model in comparison to the periodic model. As an example, the 0 K isotherm part of the equation of state for 1,1-diamino-2,2-dinitroethylene is simulated. The electronic structure of perfect and defective materials is discussed. The results demonstrate the importance of the correct inclusion of the lattice polarization into the total energy of the system. Other possible applications of the model are also discussed.

9:30 AM *AA6.3
Studies of the Properties and Reactivity of NanoAluminum. Kehong Park, sheakar Sonwane, Anand Prakash, Alon McCormick and Michael R. Zachariah; Center for NanoEnergetics Research (CNER), University of Minnesota, Minneapolis, Minnesota.

have recently, begun investigating the use of nanoaluminum for energetic applications. In this paper we discuss our experimental and computational results. Investigations using single particle mass spectrometry have been employed to study the reactivity of nanoaluminum in air as a function of particles size. These results indicate that particle melting is associated with the rapid onset of oxidation. Computational studies using both molecular dynamics and phenomenological modeling have been used to understand the properties of bare and oxide coated nanoparticles. The results have shown size dependent surface tension, high particle pressures, and the effects of surface curvature on oxidation rate. Finally we will discuss the formation of aluminum/metal oxide nanoparticle nanocomposites and evaluate their reactivity

10:30 AM *AA6.4
Reactivity of Nanosize Aluminum With Metal Oxides and Water Vapor. Jan A Puszynski, Chemistry and Chem. Eng., SDSM&T, Rapid City, South Dakota.

It has been well documented that the reactivity of nano-powders as well as bulk properties of materials derived from nano-particulates might be significantly different than those obtained from micron-sized grains. It was already demonstrated, that a rate of energy release in systems involving nanosize reactants might be increased by two to three orders of magnitude compared to reacting systems consisting of micron-size powders. There are many challenges associated with the processing of metal-oxidizer systems. The issues related to the characterization of nano-powders and their protective coatings, reactivity with moisture, dispersion and mixing of nano-reactants, as well as the measurement of the combustion characteristics in condensed phase systems will be addressed in this presentation. The primary focus of this research has been on the investigation of combustion characteristics under unconfined and confined conditions for several systems consisting of nanosize aluminum and metal oxides, such as Fe_2O_3, MoO_3, WO_3, and CuO. The effect of powder treatment, composition, and gas atmosphere on combustion characteristics in those systems will be discussed as well. The effect of aluminum powder aging, at different relative humidity levels, and the role of protective coating will be addressed as well.

11:00 AM *AA6.5
Nanofractography of Composition B Fracture Surfaces With Atomic Force Microscopy. Mary Y. D. Lanzerotti[1], Jagadish Sharma[2] and R. W. Armstrong[3]; [1]U. S. Army TACOM-ARDEC, Picatinny Arsenal, New Jersey; [2]Carderock Division, Naval Surface Warfare Center, West Bethesda, Maryland; [3]USAF AFRL-MNME, Eglin AFB, Florida.

We discuss the micron size columnar grain morphology of TNT (trinitrotoluene) in Composition B (59% cyclotrimethylenetrinitramine (RDX), 40% TNT and 1% wax) using atomic force microscopy. The fracture surface of the melt-cast Composition B was studied after mechanical failure at high acceleration (high g) in an ultracentrifuge at 46 Kg. The fracture surfacre microstructure of the TNT grains show flat TNT columns alternating with TNT columns containing "river patterns". The steps in the river patterns are found to be a few nanometers in depth. The river patterns provide information on the direction of the crack growth of the fracture surface. Possible explanations of the finely spaced TNT columnar grain morphology and the finer spaced cleavage morphology will be discussed.

11:30 AM *AA6.6
Characterization Of Nano-Sized Particles For Propulsion Applications. Grant A. Risha[1], Eric Boyer[1], Brian Evans[1], Kenneth K. Kuo[1] and Rafaat Malek[2]; [1]Department of Mechanical and Nuclear Engineering, Pennsylvania State University, State College, Pennsylvania; [2]Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania.

Energetic nano-sized particles have been shown to have a great potential for use in the aerospace propulsion applications. Currently, they have been used mainly as an energetic additive to the solid fuel or propellant formulations. Some of the unique combustion properties of nano-particles such as very fast ignition and short combustion time make them particularly valuable for propulsion systems; they can be included in solid fuels, solid propellants, or even as energetic gellant in liquid systems. However, due to the novelty of the application and rapid development of production techniques, there is no comprehensive understanding of what characteristics of a nano-sized particle are important in contributing to desirable performance and processing properties. In order to evaluate these materials for propulsion applications, a number of research studies have quantified the effect of nano-sized particle addition on different propulsion systems, including solid fuel for hybrid rockets, solid rocket propellants, and gelled rocket propellants. Many of these particles, which have been used in these studies, have data available only on the basic composition (aluminum, boron, boron carbide, etc.), average diameter, and BET surface area. In order to better understand and correlate observed combustion behavior with intrinsic material properties, the particles of interest need to be better characterized. Other properties can be vitally important to the suitability (both in processing and performance) of a particular material for propulsion and combustion applications. Some of these other properties include: - particle size distribution - particle shape - percentage of oxide vs. active content - degree of agglomeration, etc. The purpose of this paper is to report on the application of standard analysis techniques in the field of materials research to fully characterize these nano-sized materials of interest to the propulsion community. The properties listed above as well as others will be examined, tabulated, and correlated with the combustion characteristics measured in previous and current investigations for a variety of energetic nano-sized particles.
The authors would like to thank U.S. Navy-NSWC-IHD and MDA for sponsoring the research work presented in this paper.

SESSION AA7: Theory and Modeling I
Chairs: Ron Armstrong and Yuki Horie
Wednesday Afternoon, December 3, 2003
Liberty A-B (Sheraton)

1:30 PM *AA7.1
Theoretical Treatment Of Important Parameters Relating To Particle Combustion In Aluminised Explosive Systems. Les Bates, Modelling and Explosive Applications, QinetiQ, Sevenoaks, Kent, United Kingdom.

The addition of aluminium to explosive compositions for underwater use, to increase their shock and bubble energy is well known and many such compositions are in use worldwide, and continue to be studied. A new type of aluminium powder of average particle size 50-100nm, called Alex, has become commercially available, and claims have been made for its use in enhancing the performance in many energetic materials. Its potential for use in underwater explosives is an obvious area for study, its faster rate of reaction could give rise to explosives of greater shock energy and any improvement in burn efficiency could effect the bubble energy of underwater explosives. A theoretical treatment of the important parameters relating to particle combustion in explosive systems is presented. The outcome of research to compare the underwater explosive performance of a limited range of experimental aluminised compositions using Alex ultrafine aluminium, with corresponding compositions using conventional aluminium powders, is described Three explosive systems have been studied, based on, RDX/grease, nitromethane and Polyglyn/RDX. Compared to the conventional aluminised compositions, a considerable reduction in performance is seen with the nitromethane/Alex system, a small improvement is seen in the RDX/grease/Alex system, and a significant improvement is seen with the Polyglyn/RDX/Alex system. The results may be tentatively explained in terms of the reaction zone length and reaction time of the base explosive. For a liquid explosive such as nitromethane, with an exceedingly small reaction zone length, aluminium particles even as small as Alex would not react in the reaction zone of the detonation. The energetic binder Polyglyn, would confer a much larger reaction zone on the system allowing the Alex to react within or closer to the detonation reaction zone thus resulting in the recorded increased performance.

2:00 PM *AA7.2
Design of High-Energetic Materials at the Nanoscale. Purusottam Jena and Bijan K. Rao; Physics, Virginia Commonwealth University, Richmond, Virginia.

The amount of energy storage and its release in controllable pathways are two of the fundamental requirements of a high-energetic material. The novel chemistry brought about by large surface-to-volume ratio of nanomaterials provides an attractive way to design and synthesize materials that optimize the above two requirements. First principles calculations based upon density functional theory and generalized gradient approximation has been used to study the potential of

AlxLiyOz and Al(MnO4)n clusters as potential candidates for high-energetic materials. The equilibrium geometries and total energies of these clusters and their fragments are calculated to not only study the energy stored in these clusters but also their release along various pathways. For example, the binding energies of Al(MnO4)x clusters against dissociation into individual atoms are 26.24, 50.09, and 72.08 eV for x = 1,2,3 respectively. This is in contrast to the binding energy of MnO4 which is 19.65 eV. The substantial increase in binding energy either by adding Al to MnO4, or adding and MnO4 to Al(MnO4)x indicates that Al(MnO4)3 may be a potential candidate for energetic materials as well as for super-oxidizers. Similar calculations also reveal that addition of small amounts of Li to Al nano-powder helps to reduce the amount of dead weight (non-combustible Al).

2:30 PM *AA7.3
Theoretical Model for MIC Initiation and Burning.
Dennis Wilson[1], Magdy Bichay[2], Kyoungjin Kim[1], Kurt Schroder[1] and Denny Hamill[1]; [1]Nanotechnologies, Inc., Austin, Texas; [2]Naval Surface Warfare Center, Indian Head, Maryland.

The Naval Surface Warfare Center, Indian Head Division (IHD) is developing a replacement compound for lead styphnate for use in percussion primers. The replacement uses nanoaluminum plus molybdenum trioxide and is referred to as metastable intermolecular composites (MIC). The lead styphnate replacement program is in support of the green energetic effort to eliminate toxic material from the Navy inventory. The MIC material has been tested and successfully met the cartridge ballistics requirements. Sensitivity testing was also conducted for the MIC primers, and it was found to be more sensitive than lead styphnate primers and recent data from commercially available nanoaluminum demonstrated lower all-fire energy requirements. A mathematical model will be presented detailing the complex sequence of events including: the shock initiation mechanism; the molybdenum trioxide sublimation process; the aluminum particle combustion mechanism and the effect of MIC microstructure on the transport of mass, momentum and energy. The model builds upon numerous experimental and theoretical studies of aluminum particle combustion in air combined with work on combustion in high-density porous media. The goal is to: 1) interpret and explain the results of the recent tests at IHD and then 2) use the model in conjunction with experiments to optimize MIC percussion sensitivity, safety and performance. Ultimately this will be a design tool for the scale-up and manufacturing processes of MIC primers.

3:30 PM *AA7.4
Modeling Laser Generated Shock Damage and Thermo-Mechanical Chaos in Nanoparticles.
Bernard S. Gerstman, Dept of Physics, Florida International University, Miami, Florida.

Continual advances in laser technology lead to shorter pulses and higher energies. As the duration of a laser pulse shortens, different physical mechanisms become important in determining the thermo-mechanical response of an absorbing particle. These thermo-mechanical responses fall into the general category of thermal heating (temperature rise), vaporization, and shock wave formation. Our theoretical work has produced a computational model that allows the quantitative calculation of all of these responses for a laser of any pulse duration or energy, absorbed by a particle of any size. We find that for relatively long pulses, particle damage occurs most easily, i.e. at the least pulse energy, due to thermal effects. As the pulse duration shortens, explosive vaporization can dominate as the primary damage mechanism. For short pulses, shock wave production becomes the dominant damage mechanism. We describe how the relative terms of "short" and "long" pulse duration can be determined from knowledge of the thermo-mechanical properties of the absorber. Conversely, when the thermo-mechanical properties are not known, we explain how our theoretical work leads suggests an experimental technique that allows measurement of these absorber properties. This technique is applicable to extremely small particles that present difficulties for thermo-mechanical measurements. Finally, we show computational evidence of chaotic behavioral response of the absorber. This results in some laser pulse durations and energies that cause anomalously small shock waves, whereas other durations and energies cause surprisingly large and damaging responses.

4:00 PM AA7.5
Hot Spots from Crystal Size Dependent Dislocation Pile-up Avalanches in Energetic Materials.
William R. Grise[1] and Ronald W. Armstrong[2]; [1]Industrial Technology, Morehead State University, Morehead, Kentucky; [2]High Explosives Research and Development, AFRL/MNME, Eglin Air Force Base, Florida.

The precise role that dislocations play, by means of converting plastic work to heat, has long been of interest in the design of structural, load-bearing materials, but, for energetic/reactive materials is crucial to their safe-handling, and practical use in weapon or civilian applications. In this connection, Armstrong, Coffey, DeVost, and Elban showed agreement on a dislocation pile-up model basis between measured and predicted reciprocal square root of crystal size dependencies for the drop-weight impact sensitivities of RDX and CL-12 energetic crystals [1]. The dislocation-induced, localized, hot spot heating was attributed to the sudden release of a blocked pile-up. In this way, greater effect, heating-wise, was shown to occur as compared with earlier dislocation and continuum mechanics descriptions that are hard-put, quantitatively, to account for any significant rise in temperature. For metals and related materials, the culmination of such pile-up avalanches was proposed to provide an explanation of unstable shear banding behavior. A critical parameter involved in the heating mechanism is the requirement of suitably strong obstacles to block dislocation egresses until breakdown, most effectively accomplished by cleavage cracking. All indications are that energetic crystals contain fewer dislocations than are present in all other types of solids. In general, energetic crystals are relatively hard, plastically, for good dislocation reason, but also are relatively brittle, in contrast to metals being generally soft and ductile [2]. Comparative hardness measurements confirm that pile-ups involving only a few dislocations are required to cause cracking, even at conventional crystal sizes, and are associated with initiation of thermally-induced decomposition. The properties of such small dislocation numbers have associated advantages and disadvantages: on the experimental side, the influence of change in the number provides for reasonably large mechanical property variation among different crystals; and, on the theoretical side, having to deal with fewer dislocations makes prediction of their behaviors easier. And, coupling with recent interest in the initiation behavior of nanometer-size crystals, then, provides an added reason for investigating the properties of small dislocation pile-ups in small energetic crystals [3].
1. R. W. Armstrong, C.S. Coffey, V.F. DeVost, and W.L. Elban, Crystal Size Dependence for Initiation of RDX Explosive, J. Appl. Phys., 68, p. 979 (1990). 2. R. W. Armstrong and W.L. Elban, Dislocations in Energetic Crystals, Dislocations in Solids, Ed.: F.R.N. Nabarro, (Elsevier Science Publ., N.Y. 2003), Chapter 12, in press. 3. W.R. Grise, Application of Discrete Dislocation Plasticity to High-Strain-Rate Materials, AFOSR-supported NRC SFFP, Eglin AFB, FL, 2002-3.

4:15 PM AA7.6
Computer Simulations to Study the Hot-spot Initiation of HMX.
John E. Reaugh, James A. Viecelli and Nicholas W. Winter; Physics and Advanced Technology, Lawrence Livermore National Laboratory, Livermore, California.

The explosive HMX (1,3,5,7-tetranitro-1, 3,5,7-tetraazocyclooctane) does not detonate when a large single crystal is subjected to a 30 GPa shock, even with run distances as large as 8 mm. In contrast, pressed explosives made from small HMX crystals (grains) and less than 10% binder by weight detonate in 8 mm runs from shock pressures as low as 3 GPa. The voids introduced within and between crystals in pressed explosives create hot spots that lead to detonation under the influence of shock waves. We use computer simulations of HMX explosives at the grain scale to study the initiation of explosive decomposition. Our simulations use a simplified global chemical kinetics scheme of three reactions connecting four species. We show the effects of shock strength, defect shape, and shock orientation with respect to crystal elasticity and plasticity on initiation. The size of the defect also plays a role in the detonation of explosives. If the size of the defect is too small, heat conduction will quench the hot spot before a flame can propagate outward. Since the transport properties of the explosive products are pressure dependent, the size at which the hot spot is quenched is also pressure dependent. Our simulations also illuminate the pressure dependence of that size. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

4:30 PM AA7.7
Direct Evidence for Shear-induced Chemical Reactions.
John Gilman, UCLA, Los Angeles, California.

Athermal chemical reactions occur at low temperatures, and high driving rates (detonation fronts). There is a large literature reporting macroscopic shear effects, but this does not directly indicate the mechanism by which shear acts. This allows too much room for speculation. However, direct experimental results now confirm that it is bond-bending that is the most important microscopic event. One line of evidence comes from "hammer chemistry" in which adsorped monolayers of a reactant lying on a reactive substrate are bombarded with non-reactant atoms. Reaction occurs when the incident energies of the bombarding atoms reach critical values. Another line of evidence is provided when very small volumes of material are stressed, and thereby become reactive. Further evidence is provided by quamtum chemical calculations of the effect of bond-bending on the

LUMO-HOMO gaps of molecules. This is equivalent to reducing the activation energy for reaction.

4:45 PM AA7.8
Nanoscale Simulation of Shock-Induced Twinning in Diamond. Sergey V Zybin[1], Ivan I Oleynik[2], Mark L Elert[3] and Carter T White[4]; [1]The George Washington University, Washington, District of Columbia; [2]University of South Florida, Tampa, Florida; [3]U.S. Naval Academy, Annapolis, Maryland; [4]Naval Research Laboratory, Washington, District of Columbia.

We have performed molecular dynamics simulations of shock compression of diamond by using reactive bond order potential (REBO) and observed formation of extended defects in the form of twinning at moderate compressions (~10%) or piston velocities (~2-3 km/s). Twinning is the most common type of extended defects in natural and synthetic diamonds. In the simulations elastic/plastic transitions are observed for shock waves propagating along <110> and <111> but not for <100> crystalline directions. The averaged shear stress, energy, and temperature profiles are also quantitatively different. In particular, shear stress is relaxed by deformations in both transverse directions in the <111> shock wave, but not in <110> case. To investigate these differences we have calculated stress-strain relationships under uniaxial compression using both density functional theory and the REBO potential. Both methods showed good agreement for stresses and energetics under moderate uniaxial compressions corresponding to MD shock simulations of twin formation. However, under compressions higher then 15-20% (piston velocities ~4 km/sec) the REBO potential showed substantial deviations in stress response. This demonstrates the critical importance of developing robust potentials for modeling shock wave phenomena at the nanoscale.

SESSION AA8: Theory and Modeling II
Chairs: Jerry Forbes and Craig Hartley
Thursday Morning, December 4, 2003
Liberty A-B (Sheraton)

8:30 AM *AA8.1
Atomistic Simulations of Reactivity of Nanosystems - Oxidation of Aluminum Nanoparticles and Reactive Wetting of Al2O3 from Al Nanodroplets. Priya Vashishta[1], Rajiv K. Kalia[1], Aiichiro Nakano[1], Gurcan Aral[1], Timothy J. Campbell[2] and Shuji Ogata[3]; [1]Collaboratory for Advanced Computing and Simulations, University of Southern California, Los Angeles, California; [2]Stennis Space Center, Mississippi State University, Stennis Space Center, Mississippi; [3]Department of Applied Sciences, Yamaguchi University, Yamaguchi, 755-8611, Japan.

Advanced materials and devices with nanometer grain/feature sizes are being developed to achieve higher strength and toughness in metals, ceramic and composite materials and greater speeds and efficiency in electronic and defense technologies. Below 100 nm, however, continuum description of materials and devices must be supplemented by atomistic descriptions. Current state of the art atomistic simulations involve 10 million - 1 billion atoms. Multiresolution molecular-dynamics approach used in large-scale simulations will be described. Dynamics of oxidation of aluminum nanoclusters is investigated with an approach based on dynamic charge transfer among atoms. Structural and dynamical correlations and local stresses reveal significant charge transfer and stress variations, which cause rapid diffusion of Al and O on the nanocluster surface. The formation of a stable oxide scale of thickness 40A has been elucidated through the percolation of an OAl4 tetrahedral network. Variable charge MD simulation of oxidation of a flat Al surface have been carried out as a function of oxygen pressure. Reactive wetting of an Al2O3 substrate by Al nanodroplet of various shapes - spherical, cylindrical and flat - is also studied to determine the nature of interfacial sub-oxide layer and evolution of contact angle in the process of reactive wetting.

9:00 AM *AA8.2
Atomistic Measures of Deformation and Reaction Dynamics: Defect Nucleation Criterion and Strain-Dependent Reactivity*. Ting Zhu[1], Ju Li[2], Xi Lin[1] and Sidney Yip[1]; [1]Nuclear Engineering and Materials Science and Engineering, MIT, Cambridge, Massachusetts; [2]Materials Science and Engineering, Ohio State University, Columbus, Ohio.

A position-dependent criterion for dislocation nucleation has been formulated, following previous considerations by Hill and Rice, and applied to characterize the initiation of shear deformation in metallic thin films. We consider its extension to a highly strained nanorod of SiO2 subjected at the same time to chemical attack by water. Activation barriers for the analysis of stress-mediated reaction kinetics are calculated with efficient saddle-point search (Nudge Elastic Band and Dimer) methods and Molecular Orbital theory. Further extension to exothermic reactions in order to probe the strain sensitivity of shock initiation will be discussed. *Work supported by the National Science Foundation, the Air Force Office of Scientific Research, and the Honda R&D, Inc.

9:30 AM *AA8.3
Abintio Methods For The Equations Of State Of Mixtures. Sathya Hanagud, Xia Lu, Abhjit Gogulapathy and Vindhya Narayan; School of Aerospace Engineering, Georgia Institute of Technology, Atlanta, Georgia.

In most applications abinitio methods are used to obtain the potential fields between the nuclei. The potentials are then used in molecular dynamics calculations to understand the constitutive behavior of nano structured materials. One of the extensively used techniques is known as the Born-Oppenheimer Abinitio molecular dynamics where at each step potential fields are obtained by using Kohn-Sham density functional method. Other similar methods are Car-Parnillo Molecular dynamics where pseudo electron masses are used. In this paper, we present a different technique to calculate equations of states of mixtures of materials directly from abinitio techniques. The method can then be used, with some modifications, to obtain the equations of state for energetic-structural materials that contain mixtures of metal and metal oxide. Currently, such equations of state are obtained from expensive and time intensive gas gun or powder gun tests. The equations of state of mixtures are obtained from equations of state of individual components of the mixture and appropriate mixture theory. The equations of state for individual components are determined by first calculating the internal energy, from abinitio methods, as a function of the specific volume and temperature. The complete internal energy is split into three parts that consist of the cold curve energy, energy due to thermal contributions from ions and energy due to thermal contributions from electrons. Specific examples of mixtures are presented in the paper. The paper also contains discussions on modifications needed to obtain equations of state for energetic structural materials.

10:30 AM *AA8.4
Molecular Dynamics Simulations of Shock Waves in Solids. Carter T. White, Chemistry Division, Naval Research Laboratory, Washington, District of Columbia.

Processes at condensed phase shock and detonation fronts can occur on such short time and length scales that they are ideal for molecular dynamics simulations that follow individual atomic trajectories. Over the last decade our group at NRL has developed a series of potentials and methods for atomistic simulations of shock-induced phenomena in solids. A review will be given of some of our progress in using molecular dynamics simulations to link directly atomic-scale processes to the continuum behavior of condensed phase shock waves and detonations. In particular, it will be shown that even simplified models can capture such complex behavior as shock-induced elastic-plastic transitions, shock wave splitting resulting from phase transitions, and detonations. Our results indicate that the continuum view of a detonation can be meaningfully extended to the nanoscale. Recent insights gained from molecular dynamics simulations of shock waves interacting with nanoscale cracks will also be discussed.

11:00 AM *AA8.5
Molecular Dynamics Studies of Nanoparticles of Energetic Materials. Donald L. Thompson and Saman Alavi; Chemistry, Oklahoma State University, Stillwater, Oklahoma.

We are interested in developing an atom-level understanding of the structural properties and reactivity of chemically active nanoparticles. The arrangement of reactive sites, e.g., nitro and nitramine groups, at the surface of a nanoparticle may influence its reactivity and its interactions with coating materials. We have used molecular dynamics to study the structural properties of nanoparticles of typical high-energy materials with the goal of characterizing them to gain insights into chemical reactivity in and on them. We have examined nanoparticles with diameters ranging from 10 to 100 $\AA$. Various kinds of systems have been investigated, but the emphasis is on nitro and nitramine compounds.

11:30 AM *AA8.6
Theoretical Studies of Nanoscale Materials: Properties of Single-Wall Carbon Nanotubes. Brahim Akdim[1], Xiaofeng Duan[2] and Ruth Pachter[1]; [1]Materials & Manufacturing Directorate, Air Force Research Laboratory, WPAFB, Ohio; [2]Major Shared Resource Center for High Performance Computing, Aeronautical Systems Center, WPAFB, Ohio.

In our ongoing interest to gain insight into the behavior of nanostructured materials, we report density functional theory results

on the vibrational and electronic properties of single-wall carbon and boron nitride nanotubes, also taking into account the effects of intertube coupling. The calculated up-shifts in the Raman radial breathing modes (RBMs) were found to be small and systematic, and an understanding of the observed trends was obtained in terms of the effects of intertube interactions. We conclude that our approach provides a reasonable tool for accurate predictions of RBMs in C, and BN, nanotubes. Furthermore, the effects of adsorbates on field emission characteristics of single-wall carbon nanotubes, specifically the experimentally observed current suppression, or enhancement, upon O2 adsoprtion, or Cs intercalation or deposition, respectively, were also studied by applying density functional theory calculations, for capped and uncapped geometries. We discuss adsorption mechanisms that take place at the tip, also including the effects of an electric field, and highlight configurations that alter the emission properties. The calculated changes in the first ionization potentials upon adsorption were found to be consistent with the experimentally observed trends, demonstrating the usefulness of such theoretical studies in understanding the mechanisms of adsorption, and the prediction of properties related to field emission.

SESSION AA9: General
Chairs: Michael Kramer and Frank Owens
Thursday Afternoon, December 4, 2003
Liberty A-B (Sheraton)

1:30 PM *AA9.1
Nanoscale Energetics with Carbon Nanotubes. Zafar Iqbal and Yubing Wang; Department of Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, New Jersey.

Small diameter and short length single wall carbon nanotubes (SWNTs) with diameters of 0.8 nm and lengths of a few tens of nanometers, are expected to be more chemically reactive. SWNTs with diameters and lengths in this range, have been synthesized by a chemical vapor deposition (CVD) process involving the relatively low temperature disproportionation of CO using catalyst particles of selected dimensions and growth either on MgO support or within opalic structures with pre-selected interstitial dimensions, respectively[1]. The SWNTs are rapidly purified with dil. HCl to remove MgO or with dil. HF to remove the opalic spheres and release the SWNTs. The SWNTs are suspended in water containing surfactant and self assembled on microporous Teflon membranes to form thin free-standing sheets called "nanopaper". Controlled chemical functionalization/derivitization of SWNT sidewalls with energetic species - hydrogen in combination with peroxides and nitro/amino groups - was carried out by electrochemistry using SWNT nanopaper as the working electrode and precursor electrolytes. $In-situ$ Raman spectroscopy and cyclic voltammetry, and $ex-situ$ Raman imaging, infrared spectroscopy, and atomic force microscopy, were used to study the functionalization process. Nanoscale energetic initiation similar to that observed in unfunctionalized SWNTs by the RPI group [2] was carried out on the energetically functionalized SWNTs using a photoflash and a pulsed excimer laser. Photo-initiation thresholds will be discussed and compared with values obtained for pure nanopaper. The implications of these studies on the development of nanoscale energetic materials will be discussed. [1] A. Lan, Z. Iqbal, A. Aitouchen, M. Libera and H. Grebel, Appl. Phys. Lett. **81**, 433 (2002); A. Goyal, Y. Wang and Z. Iqbal, in preparation. [2] P.M. Ajayan et al, Science **296**, 705 (2002).

2:00 PM AA9.2
Ignition Requirements for Self-propagating Reactions in Nanostructured Multilayer Foils. Stephen John Spey[1], E Besnoin[2], O M Knio[2] and T P Weihs[1]; [1]Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; [2]Mechanical Engineering, Johns Hopkins University, Baltimore, Maryland.

Reactive multilayer foils consist of hundreds or thousands of alternating nanoscale layers of two or more materials that mix exothermically. When energy is applied to a section of a reactive multilayer foil, the component layers within that section will intermix and release heat. If the heat is released more rapidly than it is removed by thermal diffusion, the intermixing reaction will propagate throughout the foil. This is known as igniting the foil. The goal of this study is to nano- and micro-engineer the geometry of reactive foils to enhance their stability and thereby prevent unwanted ignition. Specifically, we fabricated and tested the ignition requirements of foils with nanoscale interlayers and microscale outerlayers. Reactive foils consisting of alternating layers of Al and Ni-7%V in a 1:1 molar ratio were vapor deposited using magnetron sputter deposition. The total thickness of the foils ranged from 60μm to 100μm, and the bilayer thickness ranged from 35nm to 55nm. An electric current was passed through the thickness of a foil sample in an attempt to ignite it. The power density of the pulse was varied by adjusting its amperage and duration until ignition was achieved. Three variants on reactive foil geometry were tested for stability. First, annealing was used to grow an intermixed region several nanometers thick between the component layers of reactive foil samples. Second, several nanometers of Cu were deposited between the component layers in other foil samples. The nanoscale intermixed regions and the nanoscale Cu interlayers impede atomic diffusion between the component layers, thereby inhibiting ignition. In the third variant, braze layers several microns thick were deposited on both sides of the foil. The braze outer layers have the effect of diffusing the current pulse before it passes through the foil, thereby increasing the total current required to ignite the foil. Experimental results and numerical predictions for ignition will be presented.

2:15 PM AA9.3
Characterization of metal and metal oxide nanopowders as additives for energetic materials. Marie Kissinger[1], Kerry Siebein[1], Charles M Jenkins[2] and Kevin Powers[1]; [1]Particle Engineering Research Center, University of Florida, Gainesville, Florida; [2]AFRL/MNME, Air Force Research Lab, Eglin AFB, Florida.

There are numerous issues involved when incorporating nano sized powders as additives in polymer melts or other high viscosity fluids. Two key characteristics include the primary particle/agglomerate size and the dispersion in the matrix. In this presentation we will discuss the characterization of several as received nanosized powders with respect to particle size, state of dispersion (dry) and potential for uniform dispersion in explosive composites. The characterization of nanopowders by modern methods of analysis such as dynamic light scattering, BET, SEM, and TEM is still far from routine, especially when such materials or their matrices are highly reactive. Issues regarding particle dispersion and rheology of the resulting mixture will also be discussed.

2:30 PM AA9.4
Synthesis and characterization of doped ferroxane nanoparticles. Maria M. F. Cortalezzi[1], Jerome Rose[2], Eliza M Tsui[1], Andrew R Barron[3] and Mark R Wiesner[1]; [1]Civil and Environmental Engineering, Rice University, Houston, Texas; [2]CEREGE, CNRS-Universite Aix-Marseille III, Aix en Provence, France; [3]Chemistry, Rice University, Houston, Texas.

Ferroxane nanoparticles are precursors to iron oxide ceramic porous membranes. The ferroxane-derived ceramics have an average pore size of 24 nm and a surface area of 80 m2/g. Previous work has shown that these membranes have a molecular weight cut off of 180,000 dalton and their permeability is comparable to commercially available membranes. The ferroxane nanoparticles were reacted with various metal acetylacetonate compounds (Zr, V, and Mn) and nitrates (Ag, Ce) and then applied to the fabrication of mixed metal oxides. The nanoparticles were deposited onto a porous substrate filtering a suspension of ferroxanes of a predetermined concentration. Upon sintering, asymmetric mixed metal oxide ceramic membranes were obtained. The materials were characterized by EXAFS in order to study the atomic environment of the iron and dopant element. EDAX was used to estimate the relative amount of dopant to iron present in the samples. IDX mapping were also applied to study the heterogeneity of the resulting ceramics. EXAFS showed that the atomic environment of the iron and dopant material was different from those in the initial compounds, thus confirming that the reaction took place. The concentration of dopant metal was in all cases between 7% and 10%. The iDX mappings show a uniform concentration of dopant throughout the material. The doped ferroxane ceramic membranes have the characteristics of the ferroxane iron oxide ceramic membranes with respect to pose size distribution, surface area, permeability, and molecular weight cut off. Furthermore, the presence of the dopant makes them candidates for reactive membranes as needed in the catalytic oxidation of organic pollutants.

3:15 PM AA9.5
TEM Characterization of Metal-Carbon Aerogel Nanocomposites. Dafei Kang[1], Ying Zhang[2], Carl Saquing[2], Can Erkey[2] and Mark Aindow[1]; [1]Metallurgy and Materials Engineering, University of Connecticut, Storrs, Connecticut; [2]Chemical Engineering, University of Connecticut, Storrs, Connecticut.

A variety of carbonaceous materials have been used as the supports for finely divided catalytic metal particles. Recently, carbon aerogels (CAs) have attracted considerable attention for this purpose because they possess a very high surface area to volume ratio. In our work, pure CAs are prepared by the pyrolysis of organic resorcinol-formaldehyde (RF) aerogels which are synthesized via a sol-gel process, followed by a supercritical CO_2 drying treatment to preserve the original pore structure. Metal is then incorporated into the carbon network by impregnation of the pure CA with organometallic precursors and subsequent reduction of these

precursors. In this paper we will describe a transmission electron microscopy (TEM) study on the structural evolution of the microporous carbon matrix and the embedded metal particles as the pyrolysis conditions, metal loadings and reduction temperatures are tailored. This work has involved the use of high-resolution lattice imaging to resolve the structure of the CAs and the metal particles on a sub-nanometer scale, and electron energy loss spectrometry (EELS) to reveal the bonding distribution in the CA.

3:30 PM AA9.6
Nanofibrous Manganese Dioxide for Volatile Organic Compounds. Huimin Chen[1], Danny Xiao[1] and Shili Liu[2]; [1]Inframat corporation, Willington, Connecticut; [2]University of Connecticut, Storrs, Connecticut.

Volatile organic compounds (VOCs) are widely used in industrial process, transportation fuels, and households. It is inevitable that some VOCs will escape into the atmosphere. Emission of VOCs will cause three major problems, including (1) increased exposure level of the population to know carcinogenic compounds such as benzene and carbon tetrachloride, (2) increased ozone concentration in the atmosphere at ground level, and (3) stratospheric depletion of the ozone layer, which alters global climate and increases exposure to UV radiation. Reducing the concentrations of VOCs will greatly improve air quality. A common method for VOC removal is catalytic decomposition. Most works have only focus on reducing VOC concentrations to a few parts per million (ppm). Very little research has been conducted on reducing the VOCs to parts per billion (ppb) levels, or less. This paper reports the decomposition of VOCs using a unique class of nanofibrous superstructure material. This open-inter-woven nanofibrous superstructure provides superb host for catalytic reactions and permits relatively easy flow of the gas stream through the structure. The nanofibrous MnO2 is highly effective in destroy more than 50 VOCs on USEPA top priority list toxic VOCs to ppb level or less at a 200 - 350C temperature.

3:45 PM AA9.7
The exothermic reaction and mechanical properties of nanostructured reactive foils. Jiaping Wang[1], Andy J Gavens[2] and Timothy P Weihs[1]; [1]Dept. of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; [2]Knolls Atomic Power Lab, Schenectady, New York.

Self-propagating exothermic formation reactions and mechanical properties were quantified for a series of Al/Ni and Al/Ti multilayer foils, using a variety of thermal, optical and mechanical measurements. The foils were sputter deposited and contain thousands of alternating layers with bilayer thicknesses ranging from 10 to 300 nm. Self-propagating reactions can be initiated in these foils with a small thermal pulse and are driven by a reduction in atomic bond energy. As atoms mix normal to the layers, heat is released and conducted parallel to the layers. If atomic mixing and energy release are sufficiently fast, then the reactions are self-sustaining. Experimental studies and numerical models have demonstrated that energy-release rates and energy densities can be controlled by varying layer thicknesses, foil compositions, and annealing procedures, prior to reaction. In this study all foils were tested at room temperature as free-standing samples, with total thicknesses ranged from 10 μm to 300 μm. The energy released from these foils and velocities of the reactions were measured using differential scanning calorimetry (DSC) and optical method, respectively. The phases in as-deposited and reacted multilayer foils were characterized using X-ray diffraction (XRD). Tensile strengths of Al/Ni and Al/Ti multilayer foils were quantified using uniaxial tensile tests and dog-bone shaped specimens with 40 mm gauge lengths. Brittle fracture was observed in these foils and the tensile strength ranged between 200 and 400 MPa.

4:00 PM AA9.8
How To Cut Reactive Foils Without Igniting Them (With Nanoscale Precision). Yoosuf Neelam Picard[1,2], Joel P McDonald[2], Joseph C Pentland[2], Hsiao-Hua Liu[2], David P Adams[3], Timothy P Weihs[4] and Steven M Yalisove[1,2]; [1]Materials Science and Engineering, Univ. of Michigan, Ann Arbor, Michigan; [2]Center for Ultrafast Optical Science, Univ. of Michigan, Ann Arbor, Michigan; [3]Sandia National Laboratories, Albuquerque, New Mexico; [4]Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland.

Recent studies using femtosecond lasers to machine a variety of materials have shown vast differences in the material modification mechanisms when compared to lasers of longer pulse lengths (nanosecond). The most striking feature common to femtosecond laser irradiated surfaces is confinement of the heat affected zone to much smaller dimensions than for longer pulse length lasers. Cutting reactive foils without igniting them can be a challenging task. Recent work irradiating NiAl multilayer reactive foils has demonstrated material removal (ablation) without ignition. We extend these studies of femtosecond laser irradiation to locally stimulate areas of a TiNi metal system surface. Reacted zones are characterized using SEM and AFM. Intensity of the radiation is varied and correlated to the ablation region characteristics.