SYMPOSIUM AA


December 1 - 4, 2003

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*Invited paper
SESSION AA1: Applications and Toxicology
Chair: Charles M. Jenkins and Walter Kozimba
Monday Morning, December 1, 2003
Liberty A-B (Sheraton)

8:30 AM *AA1.1
Potential Usage of Energetic Nano-sized Powders for Combustion Propulsion, Kenneth K. Kies, Grant A. Riska, 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 small size, they have enhanced 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 time, 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) nanoparticles can act as a gettering 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 nanoparticles. For example, several lab-scale rocket motor 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 burning rate of solid fuel by 128% in comparison to unmodified fuel or unmodified gaseous oxygen 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 Alco® powder) showed that nano-sized powders can increase the linear burning rate of solid propellants by 100%. In addition to solid fuels and propellants, spray combustion of propellants 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/liquid propellant contained in an asymptotic liquid fuel. Materials characteristics such as chemical analyses to determine the active aluminum content, density measurements, and imaging using an electron microscope have been performed on both the 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 Word, Worland, 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 characteristic 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 unconfined state will be described. An effective method that has been found is to blend with a carefully chosen inert solvent followed by a situ precipitating treatment with a desensitizing binder dissolved in the dissolvoe a dissolvable 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 trimodal distribution including very large (2000 micrometer) 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 Technology Materials Development; Kevin Walter, Chris Almstein, Doug Carpenter and David Pesiri; Technology Materials Development LLC, Santa Ana, California.

Recent results from Technology Materials Development’s supertermites program will be presented.

10:00 AM *AA1.4
Strong explosive silicon-based material. Dominik Clement, Dmitri Kovnev, Joachim Diener, Egon Gross, Nicola Kuenzer 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 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 chemical oxidizer solution. By optical means, penetration and 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 impact reaction parameters, as the initial temperature, the pressure upon release, the heating 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

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 nanosecond materials has gained intense interest recently in a wide range of applications exactly because of the new and unique properties found existing only in nanomaterials. 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 began to be known. With the small dimension of nanophase 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 energetic materials. To improve our understanding of the airbone 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 ultralight and nanomaterial 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 Calvin, 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 Ultrasmall Particles: Lessons Learned from Studies with PTFE and Al-containing Powders; Günter Oberdörster; Environmental Medicine, University of
Ukraine particles (UF, ≤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 found in very high number concentrations by combustion processes, and high levels of such particles in the ambient air may have interaction between inhaled ambient particle and adverse cardiopulmonary effects. The mechanisms related to such toxicity, however, are still unclear. We have conducted studies with laboratory-generated UF-containing flames (PFTE) elemental carbon, TiO2 and Al2O3 to gain mechanistic information related to UF toxicity. Specific examples from studies with these a UFs will be discussed and how results from those studies may be applied to human exposure and health risks of inhaled nanoparticles.


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 time- stripping technique. Observations were compared with dermal penetration of the same materials applied as conventional scale particles.

SESSION AA2: Synthesis and Characterization of Nanocrystralline Oxidizer/Monopropellant Formulations. Tom Brill, Bryce Taggar 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 on the chemical reaction rate and 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 hydrazine cyanate 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 dipiclorhate and CL-20 have been incorporated into resorcinol-formaldehyde, microsized and glycidylamide 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-metallic nano crystalline materials in binder matrices appears to hold promise as a strategy to tailor the sensitivity and performance behavior of formulation.


The utilization of nanomaterials in energetic and reactive material applications has launched alternative ideas on a previously mature field of investigation. This has led to new concepts for the use of pyrotechnics, propellants, and explosives. Entire new ways of storing and manipulating chemical energy are now being realized for a host of relevant applications. Energetic 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 advantageous 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 variety of sol-gel-derived nanometric oxidizers [e.g., Fe203, WC03, 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 thermite and gas-generating energetic nanocomposite formulations have been prepared and their distinctive properties characterized. Results and details from synthesis, characterization, and small-scale safety tests, and energy release studies will be presented.

Formation of Nanostructured Energetic Materials via Modified Sol-Gel Synthesis. Rima Tassnimbaum, 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 and both propylene oxide and some of its derivatives and added a substantial amount of the function of metal oxide and fuel molecules [e.g., dicarboxylic acid] as the gelation agents, in an attempt to control the gelation kinetics and microstructure. Methanol, ethanol, butanol, hexanol, and octanol and mixtures thereof, were studied to evaluate the time to gellation 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 molecule. Additional experiments were conducted to prove 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 bifunctional 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.

Reactive Metal Composites: Energetic "Materials by Design". Judson Ivez 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 ordnance 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 (non-aluminum) and oxygen passivated aluminum (Op-Al) using carboxylic acids as coating agents. Further, by using difunctional carboxylic acids, linear molecules with acid functionalities on both ends, we can "connect" the surfaces of two particles. We expect that we can create networks (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, N=O, 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 chemicals that when combined with the appropriate surface chemistry can survive through impact and contribute to target damage as well as numerous applications yet to be envisioned. Passionation, coaxing, and networking experiments using
Unpassivated and oxide passivated metals with various SAMs were discussed. Characterization data including SEM, TEM, TGA, and IR of prepared materials will be presented.

4:00 PM AA2.5

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 before the spontaneous reaction onset. Products are milled 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-MoO3. After empirical determination of optimum milling parameters, the reactive composites are structurally characterized by electron microscopy and diffraction techniques. Activity 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 B-Ti and B-Al 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

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 so-called chemical reactive milling. Our novel approach has proven successful in preparing metal oxide/cesium 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 material. 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 and energetic properties not seen in the microporous 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. W7405-Eng-48.

4:45 PM AA2.8

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 size 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 nanoclusters of Al and B. The first is by room temperature reduction of noble metal ions in aqueous electrolytes. These micelles are water and nafion 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, those 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 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 nanoclusters. Acknowledgement: This work was supported by the Sandin Laboratory Directed Research and Development program, the Defense Threat Reduction Agency, and the Division of Materials Science, Office of Basic Energy Research, U.S. Department of Energy under contract DE-AC04-94-AL8500. Sandia is a multi program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94-AL8500.

AA3.1

Multilayered carbon nanotubes prepared by carbon arc cathode deposit using various catalysts were characterized by scanning electron microscopy, high resolution transmission 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 graphite flakelets. Various tube morphologies are revealed by phase contrast HIMTEM images, which are associated with different catalyst behaviors involved in the tube growth. Within reasonal fluctuation range, fast Fourier transform results and XRD profiles offer essentially identical structural 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 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 thus 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 Myoe and Chuan-Jian Zheng; Chemistry, SUNY-Binghamton, Binghamton, New York.

Nanostructured materials are showing great promises for energy storage and fuel cell catalysis. The challenge today is to prepare the size and composition of the materials. This presentation discusses recent results of an investigation of the synthesis and processing protocols for the control of size and shape of metal alloy and conducting nanomaterials. 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 electronic microscopy, infrared reflection and spectroscopy and atomic force microscopy have been used to characterize the size, structural and morphological properties of the nanomaterials. 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 10/05 PER AUTHOR. C.J. ZHONG

AA3.4 Correlation of Oxidation Steps and Phase Transformations in Al-Ti Mechanical Alloys. Shiyong Xu, Miro Schmeechtz 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 Al0.5Ti0.05 to Al7Ti0.3 were synthesized as potential fuels for high energy density materials. Preliminary experiments showed increased burn rates of mechanically alloyed powders compared to pure elements. 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 thermogravimetric 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 1500°C. 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 250°C, 500°C, and 1370°C. The first oxidation step correlates with the formation of stable Al2O3 phase occurring in both pure metal powders and pure metal powders in nitrogen. The second oxidation step appears to correlate with an endothermic phase transition found to occur only in Al-Ti metastable MA powder composed of polycrystalline 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 metatization 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 model ignition of respective materials used as fuels or fuel additives in energetic materials.

AA3.5 Dependence of vertically aligned growth of carbon nanotubes on the catalysts. Nam Seo Kim, Seung Yong Bae and Jeunghlee 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 deposition of acetylene in the temperature range 900-1000°C. We also synthesized them on the silicon oxide substrates by pyrolyzing iron phthalocyanine (FePc), cobalt phthalocyanine (CoPc), and nickel phthalocyanine (NiPc) films 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 the growth rate increases with temperature for the three catalysts, which is similar with the diffusion energy of carbon in the 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 50-100 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 3-5 atomic %. The degree of crystalline perfection of the graphite sheets increases with the nitrogen content. The morphological and structural properties of the CNTs grown using Fe are better crystalline than those grown using Co and Ni. As the nitrogen content increases, the degree of crystalline perfection and the structure becomes the bamboo-like structure probably due to a release of strains.


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 absolute precision of less then 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).


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. Nanodispersion, 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 nanodispersion to measure size-specific material properties of porous NiTi produced via SHS. Indent arrays (5x5 indents; 1750µm max depth) ± 10 marker indents (250µm): Berkovich indenter tip) were positioned in a uniformly spaced grid pattern on each sample. Porous NiTi samples were examined using x-ray absorption, 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 of 4.4 ± 0.3 GPa, respectively, and did not vary with maximum indenter contact depth of 750µm (88.8 ± 8.2 and 6.2 ± 0.6 GPa) or 1500µm (87.8 ± 8.2 and 5.7 ± 0.6 GPa). The single crystal composition was Ti - 50.5 ± 0.2% Ni, compared to the SHS porous NiTi of Ti - 50.7 ± 0.4% Ni and Ti - 50.7 ± 0.4% Ni. In regions testing at 750µm and 1500µm depths, respectively. Large variance in SHS NiTi modulus and hardness likely resulted from the presence of other intermetallics but was not influenced by porosity.

Nanodispersion was able to directly measure the material properties of the SHS NiTi without being affected by porosity.


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 LiMnO2 (Li2MnO3) with an ordered-redox structure has been considered a promising cathode material in lithium-ion rechargeable batteries. In this study, nanostructured orthorhombic LiMnO2 were successfully synthesized using a newly developed
reverse-microemulsion (RME) process. To prepare α-LiMnO₂ powders with a rock salt structure, precise control of the oxygen content in the heating atmosphere was required. Moreover, Mn₃O₄ in α-LiMnO₂ was obtained at a maximum, and the reaction temperature was decreased. The reaction duration for synthesizing the desired powders was also markedly shortened via the RME process. The discharge capacities of the prepared α-LiMnO₂ 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 α-LiMnO₂ was markedly greater than that in LiMnO₂-based materials.


Nano-sized Ni₃Al particles are responsible for strengthening of the TSM75 Ni-based superalloys. 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 13 mm 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 the 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 deformation and dislocation transformation in the HAZ was studied by X-ray Laue diffraction. It was established that after cooling the deformation density is minimal in the melted zone. Approaching the final face of the solidification density sharply increases and reaches a maximal value in the HAZ at the direction of the maximal change of temperature gradient. Thereafter, 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 Berger's vector and dislocation lines along the directions [101], [121] and [110]. Within the analyzed region of 0.5 mm, these unpaired dislocations cause local rotation around the axis [110] in the plane (011).

SESSION AA4: Synthesis II
Chair: Dan Holl (Washington University)

10:30 AM - 11:00 AM


An approach related to the sol-gel route, where an aqueous solution of suitable oxides or salts is mixed with an aliphatic carboxylic acid, is known as the Pechini, or liquid mix, process. Similarly, combustion synthesis of ceramics (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 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 (150°-200° C), the reaction mixture ignites and reaction front propagates along the system, leaving behind solid product of desired 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 formation of the desired product composition. Second, the powder synthesis typically occurs at high temperatures (~800°C) for very short periods (~1 s), resulting in high purity and crystallinity. These features allow one to skip the intermediate grinding 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 nanomaterials with high surface area. This provides a range of 30-180 m²/g. Different types of oxide nanomaterials were synthesized in our laboratory using this approach, including binary iron oxides and Fe₂O₃ and Fe₃O₄ phases and complex lanthanide-based perovskites, useful for magnetic, catalytic and fuel cell applications. More importantly, based on the analysis of extensive experimental data, we have formulated basic criteria necessary to achieve high-quality nanostructured materials 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.

10:40 AM *AA4.2 Mechanical Alloying and Burning of Al-Mg Particles. C. Suryanarayanan, Devender Singh and Huei-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 much as possible an energy density of the propellant. It is known that some systems 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 material processing technique called mechanical alloying is used to make Al-Mg alloy particles. X-ray diffraction was used to examine the alloy particles before and after burning to extract the information regarding how complete the burning is and how much energy the metal propellant is releasing. The alloy particles can be made and sifted to narrow size regimes (20 to 50 μm) for better mixing with fuel. Initial results will be presented, along with data available in the existing literature. Work in progress and for the future will also be discussed.


The role of nano aluminum in performance enhancement of energetic materials, specifically solid composite propellants is well known. The burn rate is favorable. Combustion itself can be transformed into explosion. However, the effect on energy output and the safety parameters have not been addressed adequately. Unpropelled nano Al can find a place in hybrid combustion without energy loss associated with propellant incineration. We will discuss this aspect. We will also discuss briefly data on linear initiation of surface tension energy and thermal probe reaction. The advantage of nanomaterials over conventional energetic materials over nano energetic materials will be highlighted. Typically, nickel aluminate formation by solid state reaction at low temperatures (1100°C) will be illustrated.

11:20 AM *AA4.4 High-Pressure High-Temperature Sintering of Reactive Nanomaterials. Subhish M Parna, 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 retain 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 Vickers Hardness tester. Preliminary work on nano aluminum indicated that first heating and then press yield 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.

11:40 AM *AA4.5 Combustion Synthesis of NIT/LTC Composites with Controlled Porosity for Biomedical Applications. Douglas E. Burks1,2, Guglizimo Gotoi1,2, Reed A Ayers1 and John J. Moore1

Combustion synthesis, or Self-propagating High-temperature Synthesis (SHS), is increasingly 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, intermetallic, and matrix composite systems that can be used for orthopedic implants, heat exchanger and damping systems, and micro-and nano-filter applications. Functionally graded materials, both in porosity and composition, can be produced using a range of combustion synthesis techniques. Cross sectioning studies are used to identify the carbon reactant and the initial sample gage density on the general apparent porosity of the final materials has been studied and is presented within this paper. A NiTi/Gr/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 A9.6
Combustion Synthesis of Nanocomposite Al/Ni.
Emily McFarland Hunt and Michelle L. Pustoytza; 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 ranging from 100 to 106 K/s. Nanoscale reactant particles offer increased homogeneity in the resultant 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 alumina 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 an 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 aluminate composite. Results from these experiments indicate that the burn velocity of the nickel aluminate system is increased by the addition of oxide 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. The new material is formed with finer particle sizes and higher temperatures, which may prove to increase the overall strength and structure of the product.

11:45 AM A9.7
Interface and Surface Properties of Al/Ni Multilayers as Deposited and Following Volume Combustion Synthesis.
Mark Holz, D. Aurangzeb, M. Daugherty, A. Chadokh, J. Yun, J. Bergman (F. S. and M. M.); 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 this paper on the studies of the interface properties of Al/Ni multilayers and following anneals up to 760 C with 100 C intervals. Anneals duration was generally 10 min; longer anneals were performed to verify constant rates. As published previously, this study was used to probe 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 analyses was 38 and 50 nm for the two 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 200 C anneal range the interface properties remain intact, as seen from the XRR interference fringes beyond the critical angle. From anneal temperatures 360 to 400 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 layered with the same periodicity of the as-deposited layers. We interpret these fringes using the model that incorporates the difference in lateral and vertical growth rates of the alloy domains. At 600 C, the melting temperature of Al, and above the fringes completely vanish. Cross-sectional views are used to identify the nickel aluminate 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 0686490.

SESSION A9: Characterization
Chairs: John J. Gilman and Tom Russell
Tuesday, December 2, 2003
Liberty A-B (Sherraton)

1:30 PM A9.5.1
Ultrafast spectroscopy of laser-initiated nanomaterials.
Dana D. Dietl, Yang-Jiang Yang, Zhao-Qing 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 nanomaterials consisting of Al or B nanoparticles with a variety of carbon nanotubes. 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 A9.5.2
Performance and Characterization of Nanomaterials at Los Alamos.
Steven F. Sun, LANL, Los Alamos, New Mexico.

Novel properties associated with nanostructured materials, including nanomaterials, have attracted a great deal of interest recently. Measurable Intermetallic 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 as 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 (compression)), 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 A9.5.3
Ignition and Combustion Behaviors of Nanocomposite Thermite.
Michelle Pustoytza; Mechanical Engineering Department, Texas Tech University, Lubbock, Texas.

Recent advances in the field of nanotechnology have focused attention on developing nanocomposite energetic materials. This research will focus on the use of nanoscale particles to enhance ignition energy release rates and increased sensitivity to ignition. Characterization of nanoparticles is of increasing importance in the design of unique combustion behaviors of micron vs nano-composites. To this end, we have developed a new technique for analyzing particle size distributions which will be discussed in this work. 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 Fe203 composites synthesized from nano-scale reactant powders versus synthesized using solgel processing. Three nano-scale Fe203 oxidizers were compared including an aerogel, aerogel and commercial powder. Fe203. Burn rates were measured by igniting the mixture and using ultrafast 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 burn rates were performed in a cylinder of varying diameters ranging from 0.25 to 0.3125 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 burn rate, such as particle size, bulk density, and mechanical properties. A substantial increase in the burn rate was seen using nanoparticle materials, with the increase being on average 17% for each tenfold increase in particle size. The results of these initial studies indicate that these materials have great potential.

3:30 PM **A4.5.4** The Shock Infusion And High Strain Rate Mechanical Characterization Of Ultrafine Energetic Powders And Compositions, J. E. Field, W. G. Proud, M. W. Greenway, C. R. Sivior, J. E. Balzer and S. M. Walley, Cremelach Laboratory, University of Cambridge, Cambridge, United Kingdom.

This report covers current research on ultrafine energetic materials in our laboratory. The first topic concerns laser flyer shock initiation using flyer particles. Nano-sized aluminium particles have been used to generate shock waves in other materials, with the aluminium particles being heated to high temperatures above 600 °C. Nano-sized aluminium particles thus have a close relationship with high explosive properties. This report presents our experimental results on this topic and the implications for high explosive formulations.

4:30 PM **A4.5.6** Application And Characterization Of Nanoenergetic Materials In Energetic Compositions, Antoine E. D. M. von der Heijden, R. H. B. Bouna and A. C. van der Steen, Research Group Pyrotecchnics and Energetic Materials, TNO Prins Maurits Laboratory, Rijswijk, Netherlands.

As part of cooperation between several TNO institutes, including TNO Prins Maurits Laboratory, a new initiative on nano-technology was started in 2006. The main role of this initiative can be roughly divided into two areas: (1) Instrumentation for analysis and manufacture at nano-scale and (2) Nanoscale engineering techniques and their application to materials (including their applications). Currently the research at TNO Prins Maurits Laboratory is focused on the application of reactive nanomaterials to decontaminant surfaces from e.g. bacteria or toxic chemicals, the use of plasmas to generate reactive nanomaterials like carbon nanotubes, and the application and characterization of nanomaterials in energetic formulations (e.g. explosives, propellants and pyrotechnic compositions). This paper presents the latest results on the latter subject with special emphasis on volatilization processes. The results will be presented in more detail.

8:30 AM **A4.6.1** Ab-initio Calculation of the Equation of State for Organic Molecular Crystals, Frank J. Zerilli and Majin M. Kukla 4.

In recent years, a large body of research has been devoted to the determination of the equation of state of solid substances 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-dimino-2,2-dinitroethylen and 1,3,5-trinitro-1,3,5-triazacyclooctane. With relaxation of both molecular geometry and lattice parameters under 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 **A4.6.2** Embedded Cluster Model: Application To Molecular Crystals, Michael M. Kukla 4, Frank J. Zerilli 4, Peter V. Stanilov 3 and Alexander I. Schäger 3.

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 1,2-dimethylnitramine 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. Michael R. Zacherl, 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 as a function of particle size. These results indicate that particle melting is linked to the rapid onset of oxidation. Computational studies using both molecular dynamics and phenomenological modeling have been used to understanding 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/oxide/nitride nano hybrids and evaluate their reactivity.

10:30 AM *AA6.4

It has been well documented that the reactivity of nano-powders as well as bulk properties of materials derived from nanomaterials might be significantly different than those obtained from micro-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-oxide systems. The issues related to the characterization of nanosize powders and their protective coatings, reactivity with moisture, dispersion and mixing of nanomaterials, as well as the measurement of the combustion characteristics in condensed phase systems will be addressed in this presentation. The primary focus of this work has been on the investigation of the combustion characteristics under unconfined and confined conditions for several systems consisting of nanosize aluminum and metal oxides, such as Fe2O3, Al2O3, NiO, and CuO. The effect of powder treatment, composition, and gas atmosphere on combustion characteristics in these systems will be discussed. 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

We discuss the micron size columnar grain morphology of TNT (trinitrotoluene) in Composition B (50% cyclooctamethylenetetramine (RDX), 40% TNT and 1% wax) using atomic force microscopy. The fracture surface of the meltcast Composition B was studied after mechanical failure at high acceleration (5 g) in an ultracentrifuge at 46.4 K. The fracture surface microstructure of the TNT grains show flat TNT columns alternating with TNT columns containing “river patterns”. The steps in the river pattern are small and can 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. Geoffrey A. Rash1, Eric Boge1, Brian Evans1, Kenneth K. Kuo1 and Rafael Malek1. 1Department of Mechanical and Nuclear Engineering, Pennsylvania State University, State College, Pennsylvania. 2Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania.

Energetic nano-sized particles have been shown to have a great potential for use in the propulsive 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 nanoparticles 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 nanosized powder 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 vital in understanding the system as a whole 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 propellants.

The authors would like to thank U.S. Navy-NWRC-HDD and MDA for sponsoring the research work presented in this paper.

SESSION AA7: Theory and Modeling I

Chair: Ron Armstrong and Yuki Hirose
Wednesday Afternoon, December 5, 2018
Liberty A-B (Sherraton)

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

The addition of aluminum 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 aluminum powder of average particle size 541 nm 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 aluminium compositions using Alex ultrafine aluminum, with corresponding compositions using conventional aluminum powders, is described. Three explosive systems have been studied based on, RDX/greme, nitromethane and Polyglym/RDX. Compared to the conventional aluminium compositions, a considerable reduction in performance is seen with the nitromethane/Alex system, a small improvement is seen in the RDX/greme/Alex system, and a significant improvement is seen with the Polyglym/RDX/Alex system. The results may be tentatively explained in terms of the reaction zone length and reaction time of the reaction zone. Such explosives 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 Polyglym, would cause 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 improved performance.

2:00 PM *AA7.2
Design of High-Energetic Materials at the Nanoscale. Paramvir S. Jena and Biju K. Rave, 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 on density functional theory and generalized gradient approximation has been used to study the potential of
AkLiOz and Al[MnO4] in clusters as potential candidates for high-energy materials. The equilibrium geometries and total energies of the clusters and their fragments are calculated to not only study the energy stored in these clusters but also release their release along various pathways. For example, the binding energies of Al[MnO4] clusters against dissociation into atomic atoms are 20.24, 50.09, and 72.98 eV for x = 1, 2, and 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] indicates that Al[MnO4] may be a potential material for energetic materials as well as Al super-oxidizer. 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 Wagoner1, Magdy Bich2, Kyungmin Kim1, Kurt Schroeder3 and Danny Hira1, Technology, Tylor, Texas; Naval Surface Warfare Center, Indian Head, Maryland

The Naval Surface Warfare Center, Indian Head Division (IHID) is developing a replacement compound for lead styphnate for use in percussion primers. The replacement uses nanolumino 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 the primers and recent data from commercially available nanolumino demonstrated lower all-energetic requirements. A mathematical model will be presented detailing the thermodynamics 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 IHID and then 2) use the model in conjunction with experiments to optimize MIC performance: 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**

**Modelling Laser Generated Shock Damage and Thermo-Mechanical Chaos in Nanoparticles.**

Bernard S. Gersten, 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 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 model reproduces the experimental results for 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 laser 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 lends an experimental technique that allows measurement of absorber properties applicable to extremely small particles that present difficulties for thermo-mechanical measurements. Finally, we show computational evidence of the development of the behavior of the absorber. This results in some laser pulse durations and energies that cause extremely 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 Dissociation Pick-up Avalanches in Energetic Materials.**

William R. Grise1 and Ronald W. Armstrong2, 1 Industrial Technology, Missouri State University, Springfield, Missouri; 2 High Explosives Research and Development, AFRL/MNME, Eglin Air Force Base, Florida

The precise role that dissociations play, by means of converting plastic work to heat, has long been a point of interest in the design of efficient lead-base materials, but, for energetic/active materials is crucial to their safe-handling, and practical use in weapon or civilian applications. In this connection, Armstrong, Coffey, DeVost, and Ellman showed agreement on a dissociation pick-up model based on the 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 dissociation-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 in comparison with earlier dissociation and continuum mechanics descriptions that are hard-pot, quantitatively, to account for any significant rise in temperature as well as the explosive and velocity of super-oxidizer. 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).

4:15 PM **AA7.6**

**Computer Simulations to Study the Hot-spot Initiation of HMX.**

John E. Reagih, James A. Vecelli 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-tetrazocyclooctane) does not detonate when a large single crystal is subjected to a 30 GPa shock, even with run times as large as 8.1 mm. In contrast, pressed explosives made from small HMX crystals (grains) and less than 1.0% 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 greatly diminish the concentration of shock that can cause an explosive response. 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 kinetic to predict the location and shape of the oxidant wave front, the effects of shock strength, defect shape, and shock orientation with respect to crystal clarity and shape and size. The size of the defect also plays a role in the detonation of explosives. If the size of the defect is too small, the shock conduction will quench the hot spot before it 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 illustrate 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 microscopic 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-breaking that is the most important microscopic event. One line of evidence comes from "laminar" detonation where chemical reactions are taking place on reactant surfaces before reacting with non-reactant reactants. Reaction occurs when the incident energies of the bombarding reactants reach critical values. Another line of evidence is provided when very small volumes of reactants are compressed, and thereby become reactive. Further evidence is provided by quantum chemical calculations of the effect of bond-breaking on the
NOMO. Homo spots of molecules. This is equivalent to reducing the activation energy for reaction.

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

We have performed molecular dynamic 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 (~3.3 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 in (100). Crystallographic shear stress, energy, and temperature profiles are also quantitatively similar. 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 energies under moderate uniaxial compressions corresponding to MD shock simulations of twin formation. However, under compressions higher than 15-20% (piston velocities ~4 km/sec) the ReBO potential showed substantial deviations in stress response. This demonstrates the critical importance of defining robust potentials for modeling shock wave phenomena in the nanoscale.

SESSION A8: Theory and Modeling II

Chairs: Jerry Forbes and Craig Hairley
Thursday Morning, December 4, 2003
Liberty Ballroom (Sheraton)

8:30 AM *A8.1
Atomic Simulations of Reactivity of Nano-Systems: Oxidation of Aluminum Nanoparticles and Reactivity-Wetting of Al203 from Al Nanodroplets. Priya Vashishta 1, Rajiv K. Kalin 1, Aiichiro Nakano 1, Gurcan Arslan 2, Timothy J. Campbell 2 and Shuju Ogata 2, 1Collaboratory for Advanced Computing and Simulations, University of Southern California, Los Angeles, California; 2Stennis Space Center, Mississippi; 3Department 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, conventional 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 within this size range. 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 40Å has been elucidated through the percolation of an O24 tetrahedral network. Variable charge MD simulation of oxidation of a fine Al surface have been cast 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 the environment oxide layer and evolution of contact angle in the process of reactive wetting.

9:00 AM *A8.2
Atomic Measures of Deformation and Reaction Dynamics: Defect Nucleation Criterion and Strain-Dependent Reactivity. Ting Zhu 1, Ji Li 2, Xi Lin 2 and Sidney Yip 1, 1Nuclear Engineering and Materials Science and Engineering, MIT, Cambridge, Massachusetts; 2Materials 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 nanodot 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 provide a fundamental 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 *A8.3
Abinitio Methods For The Equations Of State Of Mixtures. Shalini Harcule, Xia Liu, Ahlaj Gogusulu and Vishnur Narayan, School of Aerospace Engineering, Georgia Institute of Technology, Atlanta, Georgia.

In most applications, ab initio methods are used to obtain the potential between the molecules. The potentials are then used in molecular dynamics calculations to understand the constitutive behavior of nanostructured materials. One of the extensively used techniques is known as the Born-Oppenheimer Abinitio molecular dynamics where at each step the potential fields by using Kohr-Shin method is determined. Other similar methods are CPE-Pennik 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 ab initio 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 for individual components are determined by first calculating the internal energy from ab initio methods, as a function of the specific volume and temperature. The complete internal energy is split into three parts that consist of the molar 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.

10:00 AM *A8.4

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 atomistic-scale processes to the continuum behavior of condensed phase shock waves and detonations. In particular, we will show 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 *A8.5
Molecular Dynamics Studies of Nanoparticles of Energetic Materials. Donald L. Thompson and Sharan Alavi, Chemistry, Oklahoma State University, Stillwater, Oklahoma.

We are interested in developing an atomistic 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 Å. Various kinds of systems have been investigated, but the emphasis is on nitro and nitramine compounds.
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 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 understanding the spectra of RBMs in C, BN, and SWNTs. Furthermore, the effects of adsorbates on field emission characteristics of single-walled carbon nanotubes, specifically the experimentally observed current suppression, or enhancement, upon CO adsorption, or intercalation, respectively, were studied by applying density functional theory calculations, for capped and uncapped geometries. We discuss adsorption mechanisms that include or exclude 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 Chair: Michael Kramer and Frank Owens
Thursday Afternoon, December 4, 2003
Liberty A/B (Sheraton)

1:30 PM **AA9.1**
Nanoscience Energetics with Carbon Nanotubes, Zaheer Iqbal and Yuking 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 catalytic 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 by dil. HCl to remove MgO and converted to the metallic phase by chemical reduction. The SWNTs are suspended in water containing surfactant and self-assembled on microstructured Teflon membranes to form thin free-standing sheets called "nanosheets". Controlled chemical functionalization/derivatization of SWNT sidewalls with energetic species - hydrogen in combination with peroxides and nitroamine groups - was carried out by electrophoresis using SWNT nanosheets 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. Nanosheet energetic initiation similar to that observed in unfunctionalized SWNTs by the BPM group [2], was also 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 nanosheets. The implications of these studies on the development of the nanosheet energetic material will be discussed.


2:00 PM AA9.2
Ignition Requirements for Self-Propagating Reactions in Nanostructured Multilayer Foils, Stephen John Spey, E. Bezosin 6, O M Kario 6 and T P Weilsh 6, 5Minerah Science and Engineering, Johns Hopkins University, Baltimore, Maryland; 6Mechanical 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 the section will intermix and release heat. This 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 sensitivity and thereby provide improved ignition. Specifically, we fabricated and tested the ignition requirements of foils with nanoscale interlayers and microscale outerlayers. Reaction foils consisting of alternating layers of Al and Ni-72 wt% Cu in a 1:1 molar ratio were suspended by a magnetic field on a metal plate at 150 °C. The total thickness of the foils ranged from 65 μm to 100μm, and the larger thickness ranged from 35μm to 55μm. 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 imperance 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 intermixed interlayer region for nanometer Cu layers provide atomic diffusion between the component layers, thereby inhibiting ignition. In the third variant, brush layers several microns thick were deposited on both sides of the foil. The brush outer layers have the effect of delaying the passage of current 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 Sieben 1, Charles M. Jenson 2 and Kevin Powers 1, 1 Particle Engineering Research Center, University of Florida, Gainesville, Florida; 2AFLR/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 received nano sized powders with respect to particle size, size 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 ferrozone nanoparticles, Maria M. P. Correia 1, Jerome Rose 2, Eliza M. Taul 1, Andrew R. Burton 3 and Mark R. Wiesner 1, 1 Civil and Environmental Engineering, Rice University, Houston, Texas; 2CEERGE, CNRS-Universite Aix-Marseille III, Aix en Provence, France; 3Chemistry, Rice University, Houston, Texas.

Ferrozone nanoparticles are precursors to iron oxide ceramic porous membranes. The ferrozone-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 ferrozone nanoparticles were reacted with various metal acetylacetonate compounds (Zr, V, and Mn) and nitrides (Ag, Ce) and then applied to the fabrication of mixed metal oxides. The nanoparticles were deposited onto a porous substrate filtering a suspension of ferrozone of a predetermined concentration. Upon stirring, asymmetric mixed metal oxide ceramic membranes were obtained. 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 ferrozone ceramic membranes have the characteristics of the ferrozone iron oxide ceramic membranes with respect to pore 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, Dafci King 1, Ying Zhang 1, Carl Saquing 1, Can Erkek 2 and Mark Aindow 1, 1 Metallurgy and Minerah Science Engineering, University of Connecticut, Storrs, Connecticut; 2Chemical Engineering, University of Connecticut, Storrs, Connecticut.

A variety of carbonaceous materials have been used as supports for finely divided catalytic metal particles. Recently, carbon aerogels (CA) have attracted considerable attention for this purpose because they possess a very high surface area to volume ratio. In our work, pure CA is prepared by the pyrolysis of organic precursor formaldehyde (HF) aerosol which are synthesized via a sol-gel process, followed by a supercritical CO2 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 micron-sized 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 CA 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 P.M. AA9.6


Volatile organic compounds (VOCs) are widely used in industrial processes, 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 levels of the population to known 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 concentration of VOCs will greatly improve air quality. A common method for VOC removal is catalytic decomposition. Most works have only focused 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-interwoven 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 destroying more than 50 VOCs on USEPA top priority list toxic VOCs to ppb level or less at 201 °C temperature.

3:45 P.M. AA9.7

**The exothermic reaction and mechanical properties of nanostructured reactive foils.** Jingbing Wang, Timothy P. Weil, and Andy J. Gaines. **Johns Hopkins University, Baltimore, Maryland; Knoll Atomic Power Lab, Schenectady, New York.**

Self-propagating exothermic formation reactions and mechanical properties were quantified for a series of Al/Al and Al/Ti multilayer foils, using a variety of thermal, optical and mechanical measurements. The foils were sputter deposited and contained thousands of alternating layers with bilayer thickness 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 reaction is self-sustaining. Experimental studies and numerical models have demonstrated that energy-release rates and energy densities can be controlled by varying layer thickness, foil compositions, and annealing procedures, prior to reaction. In this study all foils were tested at room temperature as freestanding samples, with total thicknesses ranging 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 self-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 length. Brittle fracture was observed in these foils and the tensile strength ranged between 200 and 400 MPa.

4:00 P.M. AA9.8

**How To Cut Reactive Foils Without Igniting Them (With Nanoscale Precision).** Yossi Nessel, Hicks, Joseph, and MacDonald. **Materials Science and Engineering, Ann Arbor, Michigan; Center for Ultrafast Optical Science, Univ. of Michigan, Ann Arbor, Michigan; Sandia National Laboratories, Albuquerque, New Mexico; 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 stress in a TiNi...