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Environmentally Benign Stab Detonators

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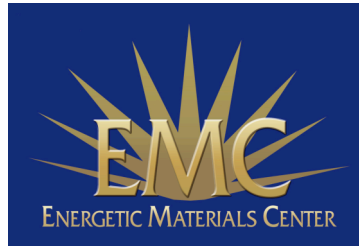
FINAL REPORT

<u>Environmentally Benign Stab Detonators</u>

SERDP Project Number: PP-1362

Performing Organization:

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List of Acronyms

LLNL	Lawrence Livermore National Laboratory
TACOM-ARDEC	Tank Armamament Command- Army Research and Development Engineering Center
IIDs	Impact initiated devices
M55	Army stab detonator
TEM	Transmission electron microscopy
DSC	Differential scanning calorimetry
μm	micrometer (10^{-6} m)
nm	nanometer (10^{-9} m)
NOL-130	Stab initiating mix component of detonator (consists of a mixture of lead azide, lead styphnate, barium nitrate, antimony sulfides, and tetracene)
mJ	millijoule (10^{-3} J)
RDX	1,3,5-trimethylene-2,4,6-trinitramine
CL-20	hexanitrohexaazaisowurtzitane
DAHA	diaminohexazido cyclotetraphosphazene

Acknowledgements

Executive Summary

Current medium caliber (20-60mm) munitions are detonated through the use of impact sensitive (stab) detonators. Both the stab initiating mix (NOL-130) and transfer charge of current stab detonators contain hazardous materials such as lead azide, lead syphnate, and barium nitrate. Alternative impact initiated devices, which do not use lead and other environmentally hazardous materials, are critically needed. The purpose of this effort was to demonstrate that both the stab initiating mix and the transfer charge could be replaced with a more environmentally acceptable solution. In this effort we examined the use of energetic sol-gel coated flash energetic nanolaminate foil nanocomposites could be used to replace the hazardous and toxic components utilized in current impact initiated devices. Initially, the desired outcome of this work is replacement of both the stab mix and the transfer charge. Developments during the course of this project necessitated changing the scope of the work. As a result the effort into a replacement for the transfer charge was strictly curtailed and the remaining effort was focused on finding a suitable replacement for the stab mix component.

Energetic nanolaminates have been known for some time. With their precise nanostructure, engineerable energy release properties, and excellent aging properties the application of energetic nanolaminate materials to problems in the field of energetic materials is promising. With a commercial supplier of this class of material present in industry a detailed study of their potential applications in the arsenal is well justified.

A key scientific question in this project involved engineering the stab sensitivity of the energetic nanolaminates to levels acceptable for many stab detonators that must function in the 3.5 to 35 mJ impact energy range. While it is well established that the propagation velocity and energy content of energetic multilayer materials can be tuned, the question of engineering the stab sensitivity to the precise levels required for the application was unknown. Another key question remained would such a stab initiating system be suitable to initiate current and future (lead-free) explosive trains and if so how would such a device's performance compare to existing ones. Finally could a new initiating train, based on new materials of this form, be integrated into the current stab detonator design without having to change the design.

This work details the stab ignition, small-scale safety, and energy release characteristics of bimetallic Al/Ni(V) and Al/Monel energetic nanolaminate freestanding thin films. The influence of the engineered nanostructural features of the energetic multilayers is correlated with both stab initiation and small-scale energetic materials testing results. Structural parameters of the energetic thin films found to be important include the bi-layer period, total thickness of the film, and presence or absence of aluminum coating layers. In general the most sensitive nanolaminates were those that were relatively thick, possessed fine bi-layer periods, and were not coated. Energetic nanolaminates were tested for their stab sensitivity as freestanding continuous parts and as coarse powders. The stab sensitivity of mock M55 detonators loaded with energetic nanolaminate was found to depend strongly upon both the particle size of the material and the configuration of nanolaminate material, in the detonator cup. In these instances stab ignition was observed with input energies as low as 5 mJ for a coarse powder with an average particle dimension of 400 μm. Optimization of the stab sensitivity of energetic nanolaminate is achieved for a material in the form of a powder, a total film thickness greater than 25 μm, a bilayer period of 20 nm, and is uncoated. Selected experiments indicate that the reacting nanolaminate can be used to ignite other energetic materials such as sol-gel nanostructured thermite, and conventional thermite that was either coated onto the multilayer substrate or pressed on it.

Live lead-free M55 stab detonators were prepared using energetic nanolamainte as the stab mix, cyanuric triazide as the transfer charge, and an Army CL-20 based formulation as the output charge. These lead free-stab detonator were demonstrated to have the required stab sensitivity (21-35 mJ) as required in current M55 detonators. The energy output of these detonators, evaluated by plate dent tests, was shown to be less than that of the current M55 stab detonators. Lead witness plates were dented to a depth of 0.76 mm with the lead-free M55 composition while the current M55 detonators have dents of ~ 2 mm.

While the lead-free M55 detonator formulations had lower energy output than current ones there was evidence that replacement of the current NOL-130 stab mix by a compact of powdered energetic nanolaminate does not affect the performance of the stab detonator. In selected experiments with the lead-free formulation a M55 detonator utilizing the energetic nanolaminate as the stab mix had the identical energy output to an M55, with the same transfer and output charge, that used NOL-130 as the stab mix. This represents a significant improvement as it implies that powderized energetic multilayer materials may be used as a replacement to NOL-130. This removes some of the toxic and hazardous components from the device.

In the course of this work it was discovered that powderized flakes (~300-500 μm) of energetic nanolaminate enhanced the stab sensitivity of the IID. This discovery dictated the unplanned development of processing method(s) to produce flakes. Initially a precision shear press was used to generate the flakes by hand. While effective this approach to powderizing the material lead to material with non-uniform particle shapes and sizes. Therefore, another "hands-free" processing method was developed that enable the preparation of flakes with uniform sizes and shapes.

Before the encouraging results with the powderized multilayers there was an effort to sensitize the multilayers using mechanical means. Specifically, the use of abrasive grit material and the use of hard structures and or meshed materials mixed in the initiating stab mix. These mechanical structures were used to induce the necessary shear and or pinching forces between the firing pin and the energetic nanolamiante to ignite the material. While this approach was

successful in sensitizing the energetic nanolamiantes towards stab initiation it was abandoned as too complex for practical integration into the existing stab detonator designs.

Objective

The coupling of energetic metallic multilayers (a.k.a. flash metal) with energetic sol-gel synthesis and processing is an entirely new approach to forming energetic devices for several DoD and DOE needs. They are also practical and commercially viable manufacturing techniques. Improved occupational safety and health, performance, reliability, reproducibility, and environmentally acceptable processing can be achieved using these methodologies and materials. The development and fielding of this technology will enhance mission readiness and reduce the costs, environmental risks and the necessity of resolving environmental concerns related to maintaining military readiness while simultaneously enhancing safety and health. Without sacrificing current performance, we will formulate new impact initiated device (IID) compositions to replace materials from the current composition that pose significant environmental, health, and safety problems associated with functions such as synthesis, material receipt, storage, handling, processing into the composition, reaction products from testing, and safe disposal. To do this, we will advance the use of nanocomposite preparation via the use of multilayer flash metal and sol-gel technologies and apply it to new small IIDs. This work will also serve to demonstrate that these technologies and resultant materials are relevant and practical to a variety of energetic needs of DoD and DOE. The goal will be to produce an IID whose composition is acceptable by OSHA, EPA, the Clean Air Act, Clean Water Act, Resource Recovery Act, etc. standards, without sacrificing current performance.

The development of environmentally benign stab detonators and igniters will result in the removal of hazardous and toxic components associated with their manufacturing, handling, and use. This will lead to improved worker safety during manufacturing as well as reduced exposure of Service personnel during their storage and or use in operations. The implementation of energetic sol-gel coated metallic multilayers, as new small IIDs will result in dramatically reduced environmental risks and improved worker and user safety risks without any sacrifice in the performance of the device. The proposed effort is designed to field an IID that is free of toxic (e.g., tetrazene) and heavy metal constituents (e.g., lead styphnate, lead azide, barium nitrate, and antimony sulfides) present in the NOL-130 initiating mixture and in the lead azide transfer charge of current stab detonators. The preferred materials for this project are nanocomposites consisting of thin foils of metallic multilayers, composed of nanometer thick regions of different metals, coated with a sol-gel derived energetic material. The favored metals for the multilayers will be main-group and early transition metals such as, but not limited to, boron, aluminum, silicon, titanium, zirconium, and nickel. Candidate sol-gel energetic materials include iron (III) oxide/aluminum nanocomposites. It should be noted that more traditional materials than sol-gel might also be used with the flash metals. The metallic multilayers undergo an exothermic transition to a more stable intermetallic alloy with the appropriate mechanical or thermal stimulus. This exothermic transition has sufficient output energy to initiate the more energy dense sol-gel energetic material, or other candidate materials. All of the proposed initiation mix materials and their reaction by products have low toxicity, are safe to handle and dispose of, and provide much less environmental and health concerns than the current composition. We anticipate that the technology and materials proposed here will be produced successfully in production scale with very competitive costs with existing IIDs, when amortized

over the production lifetime. The sol-gel process is well known and used extensively in industry for coatings applications. All of the proposed feedstock components are mass-produced and have relatively low costs. The multilayer deposition equipment is commercially available and the technology is widely used in the coating of semiconductor devices, food storage containers, and reflective windows. In addition, both the sol-gel and multilayer technologies are very versatile.   A variety of synthesis and processing variables can be tuned to change material properties such as particle or layer size or thickness, porosity, and composition can lead to materials with different properties. Using these techniques IIDs with optimized sensitivity, energy output, processing, and aging characteristics can be produced that are not as easily accessible using other nanotechnologies, in particular the use of ultra-fine grain powders.[1]

This effort attempts to demonstrate that environmentally acceptable energetic sol-gel coated flash metal multilayer nanocomposites can be used to replace current impact initiated devices (IIDs), which have hazardous and toxic components. Successful completion of this project will result in IIDs that include innocuous compounds, have sufficient output energy for initiation, meet current military specifications, are small, cost competitive, and perform as well as or better than current devices. We expect flash metal multilayer and sol-gel to be generic technologies applicable to a wide range of devices, especially in small caliber ammunition and sub-munitions.

We will replace the NOL-130 mixture with a nanocomposite that consists of a mechanically robust energetic multilayer foil that has been coated with a sol-gel energetic material. The exothermic reactions are activated in this nanocomposite are the transformation of the multilayer material to its respective intermetallic alloy and the thermite reaction, which is characterized by very high temperatures, a small pressure pulse, and hot particle ejection. The proposed materials and their reaction products consist of, but are not limited to aluminum, nickel, iron, aluminum oxide, titanium, zirconium, and iron oxide. These materials have much more desirable environmental and health characteristics than the NOL-130 composition.   In addition we will work with our DoD partner TACOM-ARDEC in identifying and testing more environmentally suitable replacement transfer charge candidates with energetic nanolaminate stab initiators.

Background

Many energetic systems can be activated via mechanical means. Percussion primers in small caliber ammunition and stab detonators used in medium caliber ammunition are just two examples.   Current medium caliber (20-60mm) munitions are detonated through the use of impact sensitive stab detonators. Stab detonators are very sensitive and must be small, as to meet weight and size limitations. A mix of energetic powders, sensitive to mechanical stimulus, is typically used to ignite such devices. Stab detonators are mechanically activated by forcing a firing pin through the closure disc of the device and into the stab initiating mix. Rapid heating caused by mechanically driven compression and friction of the mixture results in its ignition. The rapid decomposition of these materials generates a pressure/temperature pulse that is sufficient to initiate a transfer charge, which has enough output energy to detonate the main charge. This general type of ignition mix is used in a large variety of primers, igniters, and detonators.[2] A photo of an M55 stab detonator with its components identified is shown in Figure 1 below.
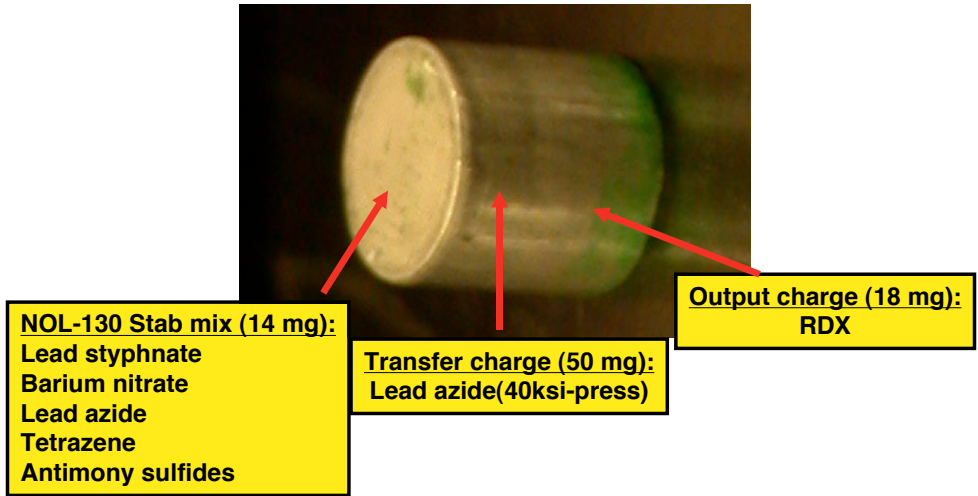
Figure 1. Photo of M55 stab detonator Al cup with initiation train and components.

Common primer mixes, such as NOL-130, are made up of lead styphnate (basic) 40%, lead azide (dextrinated) 20%, barium nitrate 20%, antimony sulfide 15%, and tetrazene 5%. These materials pose acute and chronic toxicity hazards during mixing of the composition and later in the item life cycle after the item has been field functioned. There is an established need to replace these mixes on toxicity, health, and environmental hazard grounds.

Materials and Methods

Technical Approach

Our objective is being accomplished through the development of a device(s) that consists of an energetic nanometer metallic multilayer coated with a sol-gel derived energetic nanocomposite. The proposed IIDs will be made up of a precision energetic foil of metal multilayers along with a ceramic-based energetic sol-gel coating made up of non-toxic and non-hazardous components such as ferric oxide and aluminum metal. The multilayer foils can be produced using magnetron physical vapor sputtering techniques. Both the multilayer and sol-gel technologies are versatile commercially viable processes that allow the "tailoring" of properties such as stab sensitivity and energy output. In this work, the flash metal serves as the precision igniter and the energetic sol-gel functions as a low-cost, non-toxic, non-hazardous booster in the ignition train. In contrast to other energetic nanotechnologies (i.e. mixing of nanometer powders (MIC)), these materials are safe, low cost, structurally robust, reproducible, and have excellent aging properties.

Our main interest in the sol-gel and multilayer sputtering techniques approach to energetic materials is that it offers the possibility to precisely control the composition and morphology of the target material at the nanometer scale which are important variables for both safety and reaction rates; a result that is difficult if not impossible to achieve by most conventional techniques. Such control of the nanostructure could enable the creation of entirely new energetic materials with desirable properties.

Nanolaminate materials and technology. Nanolaminates are metallic foils that are periodic in one dimension in composition or in composition and structure. They are made by alternate deposition of two or more materials. Variation is generated during the synthesis of the material, which is done atom by atom. Individual layers can be varied in thickness from one atomic layer (~2 Å) to thousands of atoms thick (>10,000 Å). Using this technology multilayer structure can be formed with microstructures and compositions that are not possible using traditional processing technology.

Multilayer structured materials can be formed by several different techniques. Physical vapor deposition, chemical vapor deposition, electrochemical deposition, electrolytic deposition, atomic layer epitaxy, and roll miling are all utilized to prepare multilayer materials. One type of physical vapor deposition involves sputtering. In sputter deposition systems atoms, or clusters of atoms, are generated in the vapor phase by bombardment of a solid source material with energetic particles. The substrate is moved past the source(s) and sputtered atoms are deposited on the substrate to form a film. A single layer of material is deposited on the substrate with each pass. The thickness of component layers, and thus it's resulting physical properties, is precisely controlled by adjusting the periodicity of substrate movement. Magnetron sputtering is one type of sputtering technique and it is the physical vapor method of choice for the semiconductor industry.

Over the last two decades researchers at LLNL have developed technology to deposit layers of atoms onto a substrate using magnetron-sputtering techniques. Alternating layers of different elements, each several nanometers thick, can be deposited on top of one another to make nanometer metallic multilayers with a thin intermixed region between the layers.[3,4] The sum of the thicknesses of two adjacent layers in the structure is referred to as the bi-layer period and is an important structural and performance parameter of the material. Figure 2 is a transmission electron micrograph of a multilayer structure with the bi-layer thickness outlined.
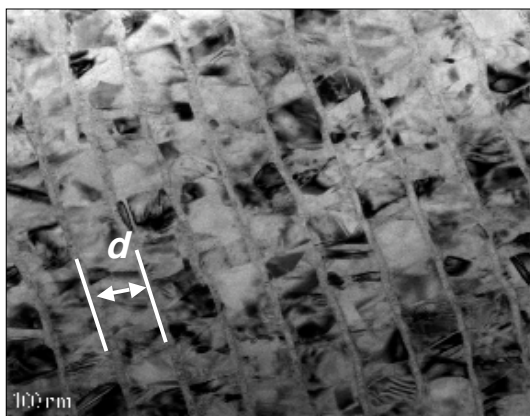

Figure 2. TEM image of a Zr/Cu nanolaminate thin film, the bi-layer thickness value is shown by the distance *d*.

One additional structural feature of energetic multilayer thin films not well illustrated by the image in Figure 2 is the pre-reaction zone. This region exists at the interface of adjacent layers of the multilayer and is made up of a thin layer of intermetallic product formed during deposition. The thickness of this region, relative to the overall period, is also very important to the energy and sensitivity of the energetic nanolaminate. There is always a pre-reaction zone in metallic multilayer structures however its thickness can be controlled.

Outer coat layers

Scheme 1. *Scheme showing the structural features of an energetic multilayer. The distance T_t is the total thickness of the multilayer, Λ is the period or the repeating structural unit of the multilayer, and δ is the prereaction zone*

A short discussion of important terminology for nanolaminate foils is now warranted and will help with full comprehension of this report. The total thickness of the foil sample is given by the distance set off by the larger set of brackets in the lower portion of Scheme 1. The distance corresponding to individual component layer thickness is set off by the smaller brackets in Scheme 1. The term referred to as the period, Λ, of the material is the distance of the repeating sub unit structure that makes up the foil. For example, in Scheme 1 Λ is the sum of the thicknesses of one Al and one Ni layer, as together they make up the repeating substructure. One additional structural feature of energetic multilayer thin films well illustrated by the image in Scheme 1 is the pre-reaction zone, δ. This region exists at the interface of adjacent layers of the multilayer and is made up of a thin layer of intermetallic product formed during deposition. The thickness of this region, relative to the overall period, is very important to the overall energy and sensitivity of the energetic nanolaminate. There is always a pre-reaction zone in metallic multilayer structures however its thickness can be controlled in many cases. Finally, many laminate materials are top and bottom coated with several layers of a single metal (in our case it was often Al layers) to assist with the film release from the substrate. All of these parameters are important as they directly relate to the sensitivity and total energy output of the synthesized foils.

The properties of the multilayers are very dependent on structure and composition, both of which can be conveniently controlled by changing reactor conditions. Certain multilayers can be engineered to be energetic: The energy being derived from the rearrangement of some heterometallic multilayers into a more stable intermetallic compound. These flash metals have

been observed to be sensitive to both thermal and mechanical stimuli.**[5-7]** The stored energy and reaction velocities of the multilayers can be systematically and independently controlled by materials selection and size scale of the layers.**[8,9]** In many cases the flash metals have the structural properties of a robust foil. This technique is very versatile as nearly all metals can be utilized to make tailored energetic multilayers and thus compositional control is vast. As the method is extremely reproducible, it is anticipated that the precision of the IIDs will be very high. Furthermore, the metallic multilayers have been shown to have good environmental stability as they are currently used as precision reflective coatings on orbiting satellites such as the Transition Region and Corona Explorer and are thus exposed to harsh environments and stresses. This is a major issue that may prove to be an insurmountable obstacle to approaches using nanometer metal fuel powders (i.e., MIC materials) in the initiating mix. The preparation of flash metals is affordable and the capital equipment and infrastructure currently exists in industry to do so. One company, RNT Foil of Hunt Valley, MD makes energetic multilayers via this process for commercial applications.**[10]** Energetic multilayers are currently used for the microwelding of electronic components. With a supplier already in the marketplace these materials have the potential to be more than a curiosity pursued in an academic or national laboratory environment.

Multilayer flash metal materials can be prepared with tailored and precise reaction wave front velocities, energy release rates, and ignition temperatures. For example, the velocity of a multilayer thin film depends on the relative thickness and composition of each multilayer structure. Reaction front velocities from 0.2-100 meters/second can be prepared reliably and precisely. Multilayer reaction temperatures between 200 and 1500 °C are observed for multilayers with different compositional and structural characteristics. Heats of reaction from 0.1-1.8 kcal/g are capable with different multilayers. There have been several reports on the modeling and characterization of these properties and the influence of structure, composition, and processing conditions on such variables. **[5-9]**

Sol-gel energetic materials. Sol-gel chemical methodology has been investigated for approximately 150 years and has been extensively employed in the disciplines of chemistry, materials science, and physics. In fact, there are few scientific fields that have not benefited, in some fashion, from the sol-gel method and its various applications. Sol-gel chemistry is a solution phase synthetic route to highly pure organic or inorganic materials that have homogeneous particle and pore sizes as well as densities. Its benefits include the convenience of low-temperature preparation using general and inexpensive laboratory equipment. From a chemical point of view, the method affords easy control over the stoichiometry and homogeneity that conventional methods lack. One of the integral features of the method is its ability to produce materials with special shapes such as monoliths, fibers, films, coatings, and powders of uniform and very small particle sizes.

The pH of the solution, the solvent, the temperature, and the concentrations of reactants used can dictate the size of the clusters, which can be from 1 nm to 1000 nm in diameter. By controlling the conditions in solution, the sol can be condensed into a robust gel. The linking together of the sol clusters into either aggregates or linear chains results in the formation of the stiff monolith. The gel can be dried by evaporation of the solvent to produce a xerogel or removed under the supercritical conditions of the pore liquid to produce an aerogel. A typical gel structure is characteristically very uniform as the particles and the pores between them are nanometer-sized. This homogeneity leads to very uniform materials properties of sol-gel derived

materials. It should be added that this is a bulk technique and in the case of atmospheric drying of xerogel coatings should require no special equipment and associated costs

Sol-gel techniques, developed at LLNL, provide a new approach to prepare energetic materials. LLNL was the first to appreciate that this methodology enables a unique way to the control of the morphology, size, and composition of components of energetic nanocomposites as well as enhancing their intimate mixing.[11-13] For the past fifteen years researchers at LLNL have developed a new economical, safe, and straightforward sol-gel synthetic routes to highly pure, high surface area, small particle size, inorganic oxides (oxidizers) and organic (fuel) sol-gel materials.[14-16] Using the sol-gel methodology structural and compositional parameters can be manipulated on the nanoscale. This has enabled the establishment of new energetic materials with new and potentially useful properties. With this method come new potential benefits of added safety, reproducibility, versatility, and low hazardous waste generation. LLNL has also developed a convenient and generic method for incorporating organic gas generating constituents into energetic ceramic/fuel metal thermite composites.

Integration of the two nanotechnologies. These two nanomaterials, nanolaminates and sol-gel materials, can be coupled to one another. One particularly attractive aspect of sol-gel methodology is that is very amenable to coating surfaces. Several mature methods such as spin-, dip-, or spray coating are currently used industrially to coat materials using sol-gel methods. The resulting materials can be relatively defect-free and durable, especially if the surface is smooth and clean. Fortunately sputtered multilayers have these characteristics.   Our objective will be accomplished by developing a device(s) that consists of an energetic nanometer metallic multilayer coated with a sol-gel derived energetic nanocomposite.[17]

Literature Background on initiation of energetic nanolaminates

The engineering of both the stab sensitivity and energy output of the nanostructured energetics is a key focus of this study. With that in mind, a short review of relevant previous work is in order. Energetic multilayers can be ignited by thermal, mechanical, and electrical stimuli. Although quite detailed analysis has been performed for the ignition of energetic multilayers initiated by localized thermal heating using a spark, laser pulse, or joule heating from electrical current, comparatively little has been reported on the parameters involved in the mechanical initiation of energetic multilayers [5-7,18] This is somewhat surprising as mechanical initiation has been demonstrated to be remarkably reliable in energetic systems for hundreds of years.[2] Mechanical ignition has some benefits over other means. It can be very reliable, low cost, and requires relatively simple components. A short review of the relevant literature on mechanical ignition of energetic multilayers is presented below.

Wickersham *et al*. first showed that the heterometallic films are initiated by mechanical impact of a tungsten carbide stylus on a zirconium/silicon bi-layer material.[5] This work revealed a strong correlation between ease of ignition and both bi-layer period and total multilayer thickness. In this report thicker multilayers with finer bi-layer periods were more easily ignited. Clevenger *et al*. report the impact initiation of nickel/amorphous silicon thin films, which are exothermically transformed to the crystalline Ni_2Si, and correlate higher reaction front velocities with a combination of finer bi-layer periods and thicker foils.[6] Self-sustained reaction was only observed in free-standing films (e.g., no substrate) with bi-layer

thicknesses less than 12.5 nm. In addition, the temperature at which Ni_2Si exothermically crystallizes was a strong function of the layer thicknesses. van Heerden *et al.* report results for the mechanical ignition of Ni/Al multilayers induced by the impact of a tungsten carbide sphere on samples positioned on a hard substrate.[18] The critical mechanical energy needed for ignition increased with bi-layer period with a minimum impact energy of ~4 mJ. It is clear from the previous work that the underlying nanostructure of the multilayer dictate its energy release and ignition properties. However there has been no detailed study as to the relationship between material parameters and the effects of stab impact initiation.

There is not a great deal known about the mechanism(s) of stab initiation of energetic materials. The most definitive study, by Chaudhri, strongly suggests that the mechanism of stab initiation is largely frictional.[19] In that system it was shown that frictional heating between adjacent energetic materials particles and not that between the steel striker tip and the energetic material particles is responsible for initiation. It was speculated that the large difference in thermal conductivity between the striker pin (metal: high thermal conductivity) and the NOL-130 mix (ionic salts and organic molecules: low thermal conductivity) leads to relatively low temperature generated at the pin particle interface relative to that generated between adjacent energetic particles subject to this force. Using that assumption, the challenge to get energetic metallic multilayers to initiate when being stab initiated by a steel pin may be difficult as both the pin and energetic material have high thermal conductivities, and therefore would be able to dissipate heat quickly and effectively, and thus would be less likely to generate local spots of high temperature to initiate a self- propagating reaction. Therefore the ability to tune the ignition threshold of these materials by structural modification is critical for this application.

In addition, direct comparison to previous mechanical ignition of energetic multilayers may be misleading, as in all cases the material was initiated on hard substrates where impact may result in pinching initiation mechanism. In a stab detonator the energetic material will be in contact with a relatively soft substrate (i.e., pressed powders).

Interaction with Army and transition plan. This is a joint effort between Lawrence Livermore National Lab (LLNL) and the U.S. Army's Armament Research Development and Engineering Center (ARDEC-TACOM) at the Picatinny Arsenal, New Jersey. The partnership with ARDEC-TACOM at Picatinny is very appropriate as they are the Army's leading research facility responsible for the manufacturing science and engineering of arsenal munitions and weapons and their production. Following successful completion of the Strategic Environmental Research and Development Program effort, the Energetics and Warhead Division of ARDEC-TACOM at Picatinny has committed support for the transition of these materials to Army systems.

Initially we focused on replacing the NOL-130 initiating mixture with a device that consists of a multilayer nanocomposite or mutilayer coated with a sol-gel energetic material. These material(s) were prepared and physically characterized at LLNL and send to ARDEC-TACOM where testing on its performance characteristics was carried out. Tests included those for impact energy sensitivity, and energy output. Feed back from ARDEC-TACOM helped dictate the alteration of processing and compositional variables for additional generations of IIDs at LLNL to improve the performance characteristics. Suitable candidate material(s) were selected and ARDEC-TACOM attempted to couple these initiating mixtures to lead azide transfer charge. Witness plate testing will be done at ARDEC-TACOM on these new stab

detonators according to specifications outlined in MIL-D-50865, MIL-D-14978, or MIL-D-70436.

The scope of work was modified after April 2005. At the recommendation of the SERDP Executive Review in April 2005 work planned, at one time under this effort, to replace the lead azide transfer charge has been eliminated. This was done as the review panel recommended that the project be ended one year early. Nonetheless, lead azide in the transition charge needs to be replaced, however replacement of the NOL-130 initiating mixture alone would be an important development for other applications such as igniters and small caliber primers. This development also curtailed efforts to study the sol-gel coated energetic nanolaminates in live detonators.

Experimental Details

Small-scale safety characterization. The response of energetic nanolaminates to friction was evaluated using a BAM high friction sensitivity tester.[20] The tester utilizes a fixed porcelain pin and a movable porcelain plate that performs a reciprocating motion. Weights are attached to a torsion arm allows for the applied force to be varied from 0.5 to 36 kg. The measure of frictional sensitivity of a material is based upon the largest pin load at which less that two ignitions occur in ten trials. The B.A.M. friction tester results are compared to an RDX calibration sample, which was found to be zero events in ten trials at 16.0 kg.

The sensitivity of energetic nanolaminates toward electrostatic discharge was measured on a modified Electrical Instrument Services electrostatic discharge tester. A single square (0.4 cm x 0.4) of nanolaminate was loaded into Teflon washers and covered with1 mm thick Mylar tape. A spark discharge of variable energy is sent from a movable electrode tip to the sample. The sensitivity is defined as the highest energy setting at which ten consecutive "no-go" results are obtained. The lowest energy setting for this instrument is 0.04 J the highest 2 J.[21]

The impact sensitivity of energetic nanolaminate foil squares were evaluated with an Explosives Research Laboratory Type 12 Drop Weight apparatus. The instrument is equipped with a Type 12A tool and a 2.5 kg weight. Squares of foil were placed on a piece of carborundum paper on a steel anvil and the weight dropped on them. Visual evaluations for "go" and "no-go" events were made by the operator. The mean height for "go" events called the "50% Impact Height" denoted DH_{50} was determined using the Bruceton up-down method.[22] Results were compared to calibrated samples of PETN, RDX, and Comp-B whose DH_{50} values are 15.5 cm, 34.5 cm, and 41.4 cm respectively.

Differential scanning calorimetry was performed on energetic nanolaminate samples using a DSC 30 instrument from Mettler Toledo. Samples were heated at 20 °C/min in a carrier gas of nitrogen flowing at 40 cm^3/min.

Screening of materials for stab sensitivity. To more efficiently test the stab sensitivity of various energetic nanolaminate stab mix a procedure was developed for testing mock M55 detonators at LLNL. The purpose of this line of experimentation was to more quickly identify promising energetic nanolaminate materials for suitable for stab initiation in the M55 and further follow on investigation and to discontinue work on less promising candidate materials. The procedure was developed and refined at LLNL with consultation from TACOM-ARDEC to ensure that the test procedure conformed to typical processing and testing procedures used in live M55 detonator evaluation.

In this procedure energetic nanolaminate with different geometries (e.g., disks or powder form) were assembled in various configurations (see Configuration sub section of Results section of this report) in the bottom of a standard M55 detonator cup, shown in Scheme 2. The total mass of energetic nanolamiante utilized in all configurations was 12-16 mg. This energetic nanolaminate configuration is then tamped down in the cup, before the surrogate powder is pressed on top of it. On top of the multilayer initiating portion of the device a surrogate powder is pressed (in the case of mock detonators) and where the transfer charge will be pressed in the case of live detonators. At LLNL both talc and lead chloride have been utilized as surrogate powders. At LLNL after loading of the surrogate material the powder was pressed at 500 psi and then an Al lid was crimped on to seal the device. To ensure that pressing of the energetic nanolaminate did not lead to ignition a selected mock detonators were opened instead of firing for visual examination to ensure no reaction on pressing. In nearly all cases we did not observe ignition of the energetic nanolamainte upon pressing of any of the components.

At ARDEC-TACOM mock detonator tests using the same configurations and methods were performed with talc as the surrogate transfer charge material. Please note that the striker pin of the stab detonator pierces the bottom end of the M55 cup shown in Figure 1 and therefore interacts with the energetic multilayer initiating mix first. The total mass of the energetic multilayer in the initiating mix is ~12-16 mg. This is only slightly less than the 18mg of NOL-130 currently used in the M55, however the bulk density of the energetic foils (5.1 g/cm^3 for Ni/Al) is significantly higher than the bulk density of the NOL-130 mix (~3.3 g/cm^3).

Tests at LLNL involved the use of a drop ball apparatus fabricated on site with some design guidance from TACOM-ARDEC, this device is shown in the photo in Figure 3.

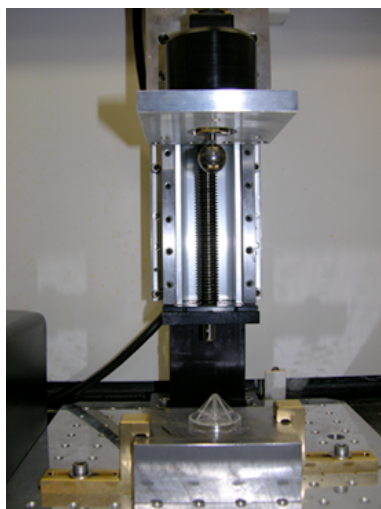***Figure 3.*** *Photo of LLNL drop ball apparatus.*

A stainless steel ball weighing one ounce (28.35 g) is dropped from an adjustable height onto the standard steel firing pin used in M55 detonators which is held in place using a disposable plastic holder provided by TACOM-ARDEC. The holder orients the pin directly above the detonator cup where the head is in position to be struck flush by the falling ball and the

tip in contact with the bottom of the cup poised to pierce and drive into the device. Once the mock detonators have been fired a visual inspection of the energetic nanolaminate stab mix is required to determine if initiation was successful or not.

Live M55 detonators were prepared at TACOM-ARDEC using the following procedure. As above, the energetic nanolaminate stab mix portion was loaded in the cup first. After that the stab mix was pressed at 10,000 psi and then visually examined to ensure that ignition did not occur upon pressing, which it did not. To follow on 20 mg of transfer charge was loaded into the detonator next followed by pressing at 10,000 psi. Two different types of transfer charges were examined here. The first was lead azide, of use in current M55 stab detonators. The second was cyanuric azide ($C_6H_3N_9$), which is a candidate green transfer charge material. Next, 20 mg of the output charge material, was loaded into the cup and then pressed at 15,000psi. The material, EDF-2C, is a US Army formulation that contains the high explosive CL-20 as its energetic component. The composition of the green stab detonator was formulated to have the same total energy content as the current M55 stab detonator. Finally, an aluminum closure disk was added to the cup and it was crimped closed. The live M55 detonator tests were performed on the drop ball apparatus at TACOM-ARDEC. In some experiments lead witness plates were used to measure the output of the detonator as is described in military standards MIL-D-50865, MIL-D-14978, and MIL-D-70436. Laser profilometry was employed at LLNL on the dented witness plates to evaluate the dent profile and maximum depth. Data from witness plate testing was compared to that obtained from M55 detonators loaded with the same transfer and output charges with the current standard NOL-130 as the stab mixture.

Formulation of energetic coatings. Two different approaches were applied to coating of energetic nanolaminates with thermite-based materials in an attempt to boost the overall energy output of the stab mix. Using these two approaches a total of three different energetic films were formulated and applied to energetic nanolamaintes resulting in energetic coatings whose thicknesses could be varied from 5 microns up to 100 microns. In the first approach sol-gel chemical methods were applied to prepare nanometric oxidizer/fuel composites that were then coated onto nanolaminate substrates. The energetic sol-gel solutions were generated using previsously reported methods and materials.**[11-13]** Using sol-gel methods coatings of two different thermite compositions, Fe_2O_3/Al and WO_3/Al, were successfully coated onto energetic nanolaminates. This was accomplished using three different application methods, spin-, dip-, and spray coating. Utilizing these methods dried coatings as thick as 5 microns were obtained. IN addition both thermite compositions were formulated with both ultra fine-grained (UFG) nanometric Al and micron sized (2 microns) H-2 aluminum.

In as second approach a thermite-type material, with added polymer for gas generation, was formulated and coated onto energetic nanolaminate surfaces using a commercial available thixotropic coating agent. The thermite-type material was composed of commercially available blended powders of (all amounts are weight percentages) 34 % Fe_2O_3 (5 μm) 30.5 % Ni (3 μm), 28.5 % Al (2 μm), and 7% Zonyl^{TM} (fluoropolymer). Using this approach, coatings with thicknesses between 5 μm and 100 μm were deposited on energetic nanolaminates by dip-coating and painting methods, respectively.

Fabrication of energetic nanolamiantes. A number of energetic nanolaminates were prepared at LLNL for this study. Nanolaminates were fabricated using magnetron sputtering (a physical vapor deposition process). A more detailed technical description of the method and its

associated parameters can be found elsewhere.[23] Various deposition parameters were varied to prepare different energetic materials with distinct bi-layer spacing and total thicknesses. In general bi-layer spacing was varied from 18 nm to 62 nm and the total film thickness was varied from 9 μm to 55 μm. Two different energetic multilayer compositions were studied here. One was a bimetallic structure consisting of alternating layers of aluminum metal and a nickel-vanadium alloy (93 wt.% Ni, 7 wt% V). The other composition consisted of aluminum and Monel 400 alloy (66.5 wt.% Ni, 31 wt. %Cu, 2.5 wt % Fe, trace amounts of C, Mn, Si, and S).

   Processing of energetic nanolaminates into different forms. During the course of the project it became clear that there were certain advantages to manipulating the form of the energetic nanolaminate. To complete the stated objective of this project it became necessary to transform the form of the energetic nanolaminate in many cases. Processing of an energetic material into a useful or optimized form is a common task. Rarely does an energetic material go straight from the final synthesis step into an application (i.e., pressing or formulation of high explosives) and energetic nanolaminates are not unique here.
   After fabrication the energetic nanolaminate was in the form of a 4" diameter disk on a substrate. From that first form factor the materials have been processed into free-standing foil disks, strips, and a coarse powder. Cutting of the fabricated piece into strips or powder was most effectively performed using a precision shear press. In the process free-standing foil pieces are cut into long fine strips of material using a hand shear press. The fine strips are then passed through the shear press several times to produce a powder of multilayer pieces. Disks of energetic nanolaminate were formed with diameters from 0.125 to 1 inch using a precision punch and die set. Physical manipulation of energetic material especially introducing shear forces is cause for careful techniques. Punching and shearing of the material with precision shim punches at room temperature appears to be very effective for safe handling. It was observed that unintended ignitions of laminate while punching or shearing were relatively rare as long as the area around the blade on the shear and the punch/die interface were frequently cleaned and kept relatively debris-free. Ignitions tend to occur much more frequently when a punch has been used several times without cleaning.   Cleaning of the shear blade and punch and die edges was effectively performed with an ethanol wipe.

Results and Accomplishments

Energetic Nanolaminate Fabrication

   Preparation of energetic multilayers with varied structure to enhance mechanical sensitivity. Of specific interest to this project are the structural parameters of the nanolaminate and how they affect stab sensitivity and energy output of the device. Qualitative reasoning, suggests that by decreasing the thickness of individual layers in the nanolaminate the stab sensitivity of the material would increase. The rationale for this is that with decreasing bi-layer thickness (see Scheme 1) the average diffusion distance between reactant species in adjacent layers decreases. The bi-layer thicknesses of the foils can be readily and precisely controlled via magnetron sputtering. However the influence and extent to which each of the structural parameters affects the stab sensitivity is not known. Therefore a series of nanolaminates with

varied structure and composition have been prepared at LLNL for this project. A summary of the energetic nanolaminates, with their structural and compositional features as well as small-scale safety data, fabricated at LLNL is given in Table 1 below.

Table 1. Summary of energetic nanolaminate specimens, their structural parameters, and small-scale safety characteristics that were examined in this effort.

Sample	Thickness (μm)	Bi-layer Period (nm)	Coating	Total energy (J/g)	DSC Exo Onset (°C)	Min. Spark Energy (mJ)	Min. BAM Friction (kg)	DH_{50} (cm)
Al/Ni(V)-1	24	16.9	No	844	215	40	4.8	20
Al/Ni(V)-2	NA	18.2	No	824	215	40	3.6	12
Al/Ni(V)-3	25	13.6	No	842	215	40	3.4	14
Al/Ni(V)-4	31	NA	No	847	215	40	4	13
Al/Ni(V)-5	9	19	Yes	593	215	40	12.8	73
Al/Monel-1	NA	NA	Yes	NA	NA	40	10.8	168
Al/Monel-2	NA	NA	Yes	830	195	90	9.6	50
Al/Monel-3	NA	18.2	No	895	195	40	4.5	12
Al/Monel-4	55	20.2	No	734	195	40	4.5	6
Al/Monel-5	26	62	Yes	1085	195	40	12	>177
Al/Monel-6	12	25	Yes	997	195	40	12	64
Al/Monel-7	13	11	Yes	594	195	40	4.2	168
Al/Monel-8	18	13	Yes	768	195	40	4.8	13

Through stab sensitivity testing, reported in the 2004 and reconfirmed in 2005 with a new modified drop-ball apparatus, it was determined that the early generations of multilayers reported in Table 1 were not suitably sensitive for use in M55 stab detonators. Therefore a need existed to enhance the mechanical sensitivity of energetic multilayers.

      All subsequent generations of nanolaminates reported in Table 1 were prepared with the expressed goal of increasing the sensitivity to impact and friction stimulus and energy output relative to those reported in Table 1. To achieve that, both structural and compositional parameters were varied. In all the cases in Table 1 the repeating bi-layer thickness (see Λ in Scheme 1) was reduced relative to previous materials. Also the newer materials in Table 1 were not over-coated with a final finish of several metallic Al layers, as was done previously.

      With no protective overcoat these materials will be more sensitive to mechanical stimulus, as no input energy will be required in the deformation and mixing of adjacent layers that have no heat of alloying (e.g. the mixing of adjacent Al capping layers). In addition, capping layers may also act as an inert substrate for the multilayer that acts as a heat sink that, under a given set of conditions, can act to quench the self-propagation of reacting foils.

     Small-scale safety evaluation. Small scale testing of energetic materials is done to determine their sensitivity to various stimuli including friction, spark, impact, and an elevated thermal environment. These tests are of extreme importance for several reasons, but mainly to

establish important parameters for safe handling, processing, and storage. An energetic material's small-scale safety data are often the first properties that are considered when evaluating a material for a particular purpose. Table 1 contains a summary of the small-scale safety test results and structural parameters for the selected energetic multilayers examined in this study.

There are several important conclusions that can be drawn from the data in Table 1. In general, regardless of structure, all of the energetic nanolaminates have very a similar decomposition onset temperature of ~ 200 °C. While this temperature is lower than some traditional energetic materials it does not preclude their use in new IIDs. Another common trend, amongst all nanolaminates considered, from this data is the high sensitivity to spark stimulus they all displayed. As can be seen, regardless of structural parameters spark stimulus is a hazard that must be considered when dealing with these materials. In fact, the ultimate lower spark sensitivity limit was not realized from these tests as the spark apparatus at LLNL does not measure below 0.04 J of energy and all of the energetic nanolaminates showed spark sensitivity at that level. It is not surprising that the energetic multilayers are spark sensitive as there are numerous studies that use spark stimulus as a method of ignition.[3,4] While this is an important hazard to consider it is one that has been dealt with effectively with current IID component materials. For example, both lead azide and lead styphnate, two of the ingredients in the stab mix that the energetic nanolaminates seek to replace are extremely spark sensitive with spark sensitivity levels of 0.0002 J and 0.0009 J, respectively. **[24]** From the data presented in Table xx it does not appear that the structure of the multilayer has any effect on its spark sensitivity. Alternatively, both the impact and friction sensitivities of the energetic nanolamiantes studied here were dependent on their respective nanostructures.

As a whole, the nanolaminates with thinner layers of reactant materials and no overcoats are much more sensitive to impact and friction than those with thicker layers and capping layers of aluminum. This point is effectively illustrated by considering the color-coded bar graphs in Figure 4.

a)

Drop Hammer results for coated and uncoated energetic multilayer materials
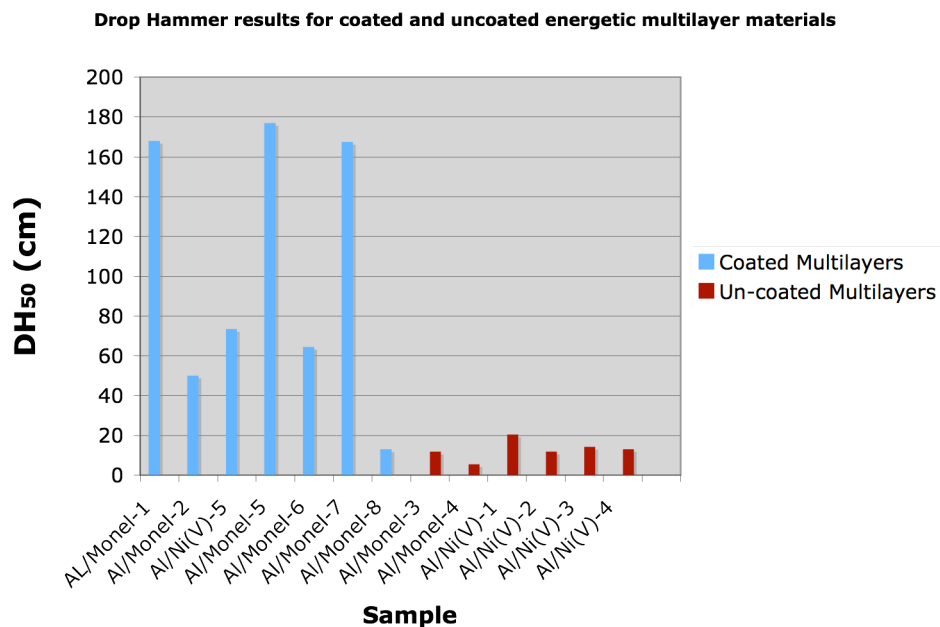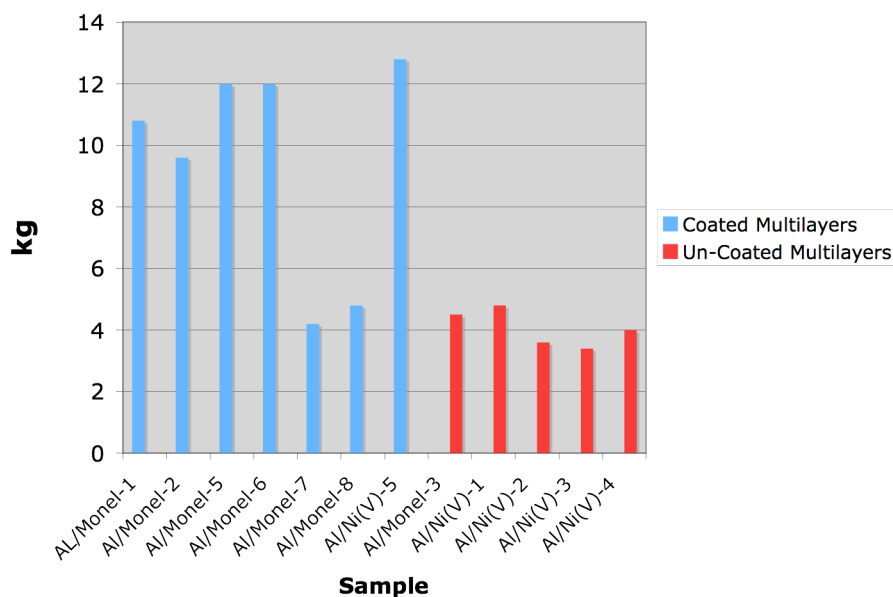
b)

Figure 4. Results of drop hammer impact a) and B.A.M. friction testing on energetic multilayer samples with and without coating layers.

From the data presented in Figures 4a and 4b it is very apparent that the presence of overcoating layers on the outside of the nanolaminate are extremely important to the impact and friction sensitivity of the multilayers. Sputter coated thin films are occasionally coated on the outer layers to help with post deposition release from the substrate. It was expected that the presence or absence of these layers would affect the ignition properties of the thin films. These are interesting results as they indicate in a semi-quantitative manner that the sensitivity of these energetic materials can be engineered. The safety characteristics of the material can potentially be tailored to the necessary levels for a particular application.

For comparison, lead azide displays a $DH_{50} = 4$ cm using a similar drop hammer apparatus to that at LLNL.[24] From the data in Table 1 and Figure 4 the selected energetic nanolamaintes have impact sensitivities that range from values on the order of that for lead azide to several times that, however none were more sensitive than lead azide to impact.

Friction is the hazard most universal in handling and processing energetic materials. It is nearly impossible to eliminate as inherent tasks of handling, pouring, mixing, and pressing induce sliding, rotating, and scraping actions on the energetic material. While being friction sensitive to the BAM level of 4-6 kg these selected energetic nanolaminates are less sensitive to friction than lead azide which has registered detonation at 20 g on the BAM apparatus, according to published accounts.[20] Although it is important to emphasize that with the energetic

nanolaminates individual single free-standing coupons of foil were tested for friction sensitivity. No BAM friction tests were run on the powderized nanolaminate.

Differential scanning calorimetry of selected energetic multilayers indicates very desirable aging characteristics. One of the significant issues with the use of nanomaterials in energetic applications are their aging characteristics. The large surface area inherent in most nanomaterials enhances surface oxidations reactions, especially with fuel metals like aluminum and zirconium, and can lead to rapid degradation of energy and performance.**[MIC refs/MRS meeting]** Energetic multilayers are nanostructured, contain such fuel metals, and have high *interfacial* surface contact areas therefore, their exposure to surface species and resultant vulnerability to them is quite low. Previous generations of energetic nanolaminates have shown excellent stability on storing under ambient conditions up to 10 years. These energetic materials had several capping layers of aluminum that may protect the underlying multilayer structure. As this effort has focused on enhancing the stab sensitivity of the materials through removal of these layers it became relevant to examine the stability of the uncoated energetic multilayers. Differential scanning calorimetry results (DSC) have demonstrated that this stability is excellent. Figure 5 contains the DSC scans of the same uncoated Al/Ni(V) nanolaminate material. In Figure xxa the sample was had been stored under ambient conditions for one month after fabrication and the scan in Figure 5b was after 14 months. One will note no difference in the total energy of the two foils indicating robust aging characteristics of the uncoated foil. Similar behavior was observed for uncoated Al/Monel multilayers also (see Figure 6).
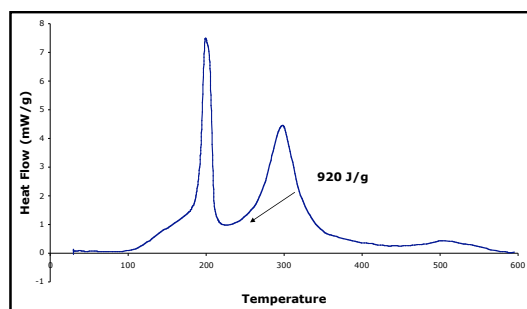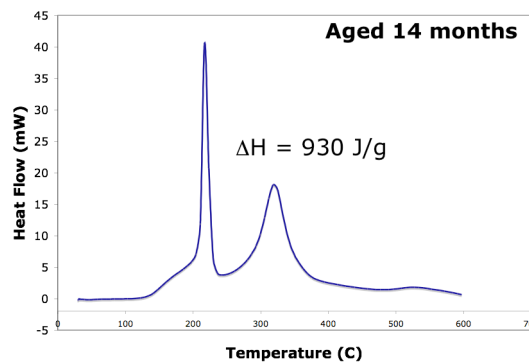
a)   *b)*

Figure 5. *DSC traces for uncoated Al/Ni(V) films right after fabrication a) and after 14 months of storage under ambient conditions.*
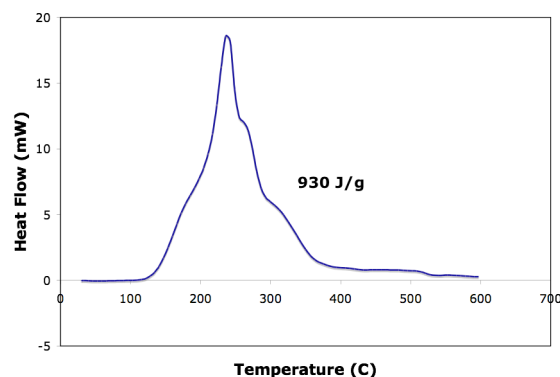
Figure 6. *DSC of uncoated Al/Monel energetic multilayer 14 months after fabrication.*

From the data presented here it appears that uncoated energetic nanolaminates have excellent aging properties under ambient conditions when compared to other energetic nanocomposites.**[1]**

This section of the final report summarized our studies of the thermal properties and safety characteristics of energetic nanolaminates with careful consideration to factors relevant to the handling and processing of energetic materials. The study was done utilizing metrics accepted by the energetic material community. It must be recognized that this set of tests have been designed for inorganic and organic explosive materials and not for energetic metallic multilayers. While we believe the results of these tests are instructive and give a good idea of the sensitivity of the materials, consideration of the results should be done with extreme caution. As these materials gain more attention in energetic materials research and applications more refined models of ignition and more suitable sensitivity testing may be developed. For the present, this report constitutes one of the most comprehensive studies of the small-scale safety properties of these energetic nanomaterials.

As small-scale safety testing revealed, the hazards associated with the handling and processing of energetic nanolaminates must be recognized and respected. Thermal stability of the candidate energetic nanolaminates is acceptable. The impact and friction sensitivity of the material was shown to be a strong function of the multilayer structure and could be engineered to be quite sensitive by those metrics. Alternatively the spark sensitivity of the energetic nanolaminates is extreme and for the selected materials tested here independent of multilayer structure. Nontheless these materials are candidates to replace the stab mix that contain lead azide and lead styphnate, both of which are primary explosives and by nature present extreme and challenging handling and processing conditions. Therefore the implementation of energetic nanolaminates into the pre-existing processing procedures for stab detontors would not necessitate a major shift as there are extreme hazards already accounted for in the process.

**Processing of Energetic Nanolaminates**

Development of methods to prepare powderized energetic multilayer. Experimental results from early in 2005 indicated there were significant advantages to "powderizing" energetic multilayers. Up to that point in the study energetic multilayers were utilized as monolithic freestanding foil disks and or strips with multi-millimeter dimensions. As the materials are deposited as single continuous films some thought and development has gone into the reduction of the film to a powder and classification of that powder.

The term "powder" used in the rest of this report requires some discussion as it is not a powder in the classic sense. Reducing the energetic multilayer to a "powder" involves cutting and or shearing the sample into small square or rectangular pieces (with sub-millimeter dimensions). The pieces are still multilayers with large x and y dimensions relative to the foil thickness (tens of microns). For some time, the reduction of multilayer monoliths to powder and subsequent classification has been done by hand. The process is summarized pictorially in Figure 7.
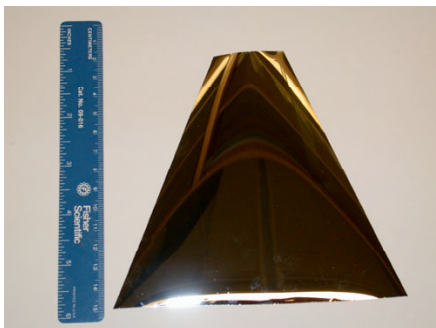
a)   *b)*
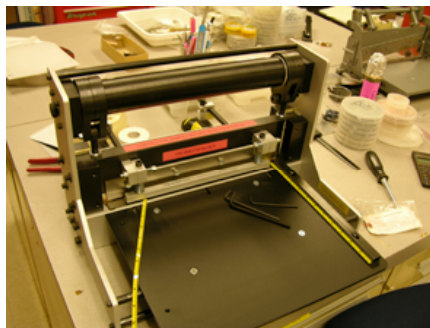
c)   *d)*

Figure 7. *Photos summarizing the process of reduction of multilayer thin films to powdered material. Top left sheet a) is cut using the precision shear press b) into long fine thin strips of material (~2-10 cm long) which is then repeatedly passed through the shear press to produce an energetic multilayer powder d).*

In the process free standing foil pieces like that shown in Figure 7a are cut into long fine strips of material using a hand shear press like that shown in Figure 7b. The fine strips are then passed through the shear press several times to produce a powder of multilayer pieces. While this processing was effective in producing powders with desirable characteristics it is not very efficient as it is labor intensive and produces material with non-uniform particle sizes and shapes from batch to batch. Once a powder of energetic multilayers is produced from the hand process in Figure 7 it consists of pieces with different particle sizes. As particle size distribution is a strong factor in the performance and behavior of energetic materials attempts to control and classify the powder have become important. Through the use of standard sieves a powder from the process is classified on the basis of particle size dimensions. Clearly the process described here would be problematic for any large-scale production of the material. However this we have taken steps to optimize the process and material.

Recent developments have streamlined the powder production process and allowed production of powders with optimal particle dimensions and have uniform size distribution. Photos of the uniform powder samples are shown below in Figure 8.
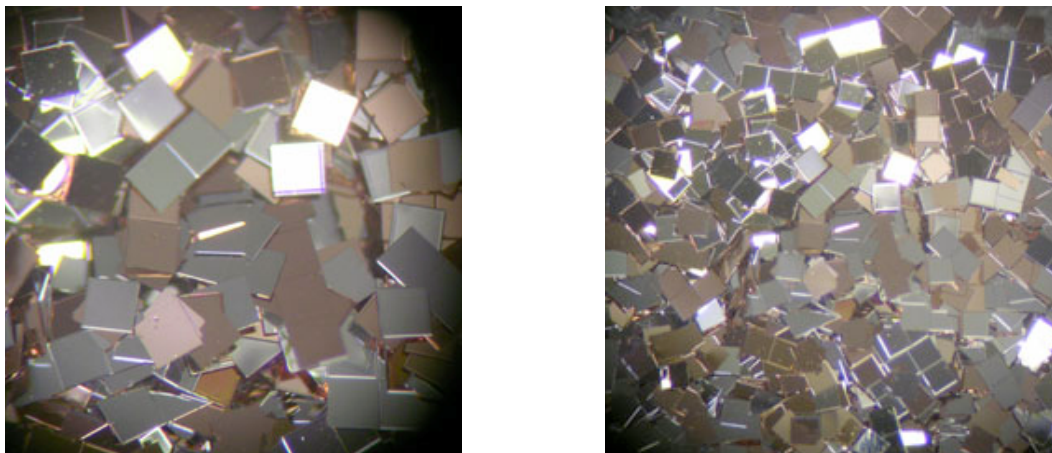

Figure 8. Photos of uniform powderized Al/Ni(V) nanolaminate. The particles are 300 μm x 300 μm.

Uniform particle size and shapes of the energetic nanolaminate will result in powders with more precise and reproducible response to stab stimulus.

Evaluation of Stab Sensitivity of Energetic Nanolaminates

The critical metric used in evaluating the efficacy of different materials as impact-initiated devices is impact energy. This can be envisioned as the amount of mechanical energy needed to cause the material to ignite/decompose. The firing energy for stab initiators is determined by a drop-ball test. In such a system a ball of a given weight is dropped from varying heights onto a centered firing pin that pierces the initiator mix. Many tests are run and the data is

reduced to firing energy versus probability of initiation.**[2]** The sensitivity of IIDs to the drop ball test is reported in units of inch/ounces. That number can be thought of as how high a one-ounce ball needs to be dropped from to ignite the device. Most stab initiators function with high reliability between 0.5 and 5 in./oz (3.5 to 35 mJ of energy). Percussion primers have higher firing energies, in the range of 18-60 in./oz (125-420 mJ of energy).

Using procedures described earlier in the report the stab sensitivity of several different multilayer materials were evaluated in M55 mock detonator sample configurations. Since the tests were done on mock detonators "go" and "no-go" results were determined by visual inspection of the initiating mix after firing. This evaluation is quite straightforward as the visual appearance of the materials after reaction is drastically different than before. Figures 9 and 10 illustrate this point well.
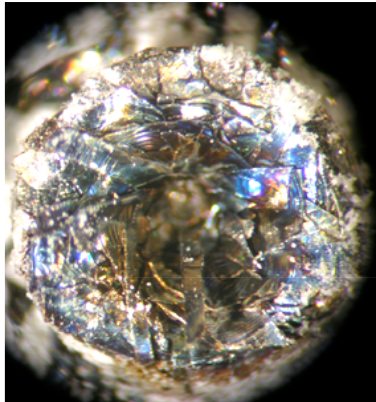
a)   *b)*
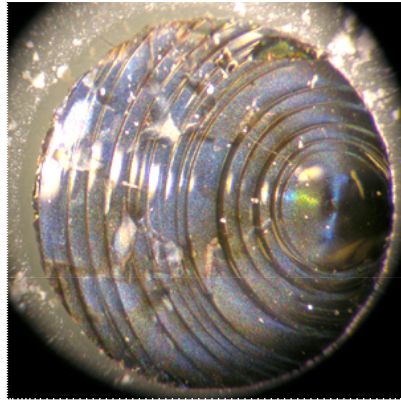
Figure 9. *Photos of successful (go) reacted multilayer energetic foils materials. These materials were initiated in a M55 mock detonator configuration with stab input.*

Powder from the stabbed and reacted foils tend to fuse together into one large plug that has been significantly deformed and is shown in Figure 9a. In addition, the reacted materials display distinctive coloring possibly due to birefringence and often display ripples due to thermal wave propagation.

The appearance of the stabbed un-reacted multilayers is much different. This is well illustrated in Figure 10. The photo in Figure 10a shows a multilayer disk that has been perforated by a firing pin without reaction of the multilayer, and that in Figure 10b is that of un-reacted powder. One can see that the material has not been significantly deformed, and appears to have the same reflective properties as the starting multilayers.
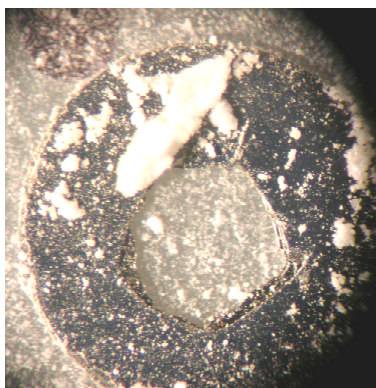
a) *b)*

Figure 10. *Photos of energetic multilayer disks a) and powder b) that has been stab impacted but did not initiate.*

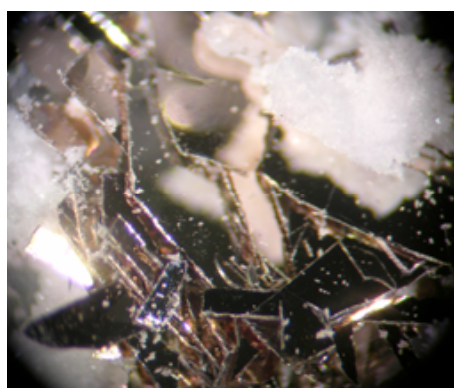As our initial testing unfolded the main technical challenge that arose was the sensitization of the energetic nanolaminate to acceptable levels for stab detonators. To be a suitable replacement, the stab mix must be sensitive enough to be initiated with an input energy in the range of 0.5-5 in./oz. (3.5 to 35 mJ). This was a serious issue, as until it was overcome important future milestones in the areas of application testing and validation would be delayed or not met. This was successfully accomplished using uncoated energetic multilayers in a powder form both with and without the use of mechanical sensitizers.

It was immediately recognized that the use of powders of energetic nanolamainte in mock M55 stab detonator testing at LLNL had dramatic results on the stab sensitivity of the device. From early qualitative observations it was apparent that the powderized form of the material enhanced the stab sensitivity of the mock IIDs to a very significant extent. Initially powders like those shown in Figure 7d were utilized. These powders are typically made up of particles or shards of material with a broad range of sizes and geometries and thus were not very uniform. Attempts to better characterize the powders and obtain more reproducible stab initiation results led to size sorting of the sheared material. This was performed using a series of Tyler U.S. standard sieves and collecting the resulting size fractions of material. Selected fractions with relatively uniform particle sizes were tested for stab sensitivity. A summary of their initiation impact energy versus average particle size is shown below in Figure 10. The data was obtained from an uncoated Al/Monel 400 multilayer material with a thickness of 55 μm and a bi-layer period of 20 nm (Al/Monel-4 in Table 1) tested in configuration B (see Scheme 2 later in report).
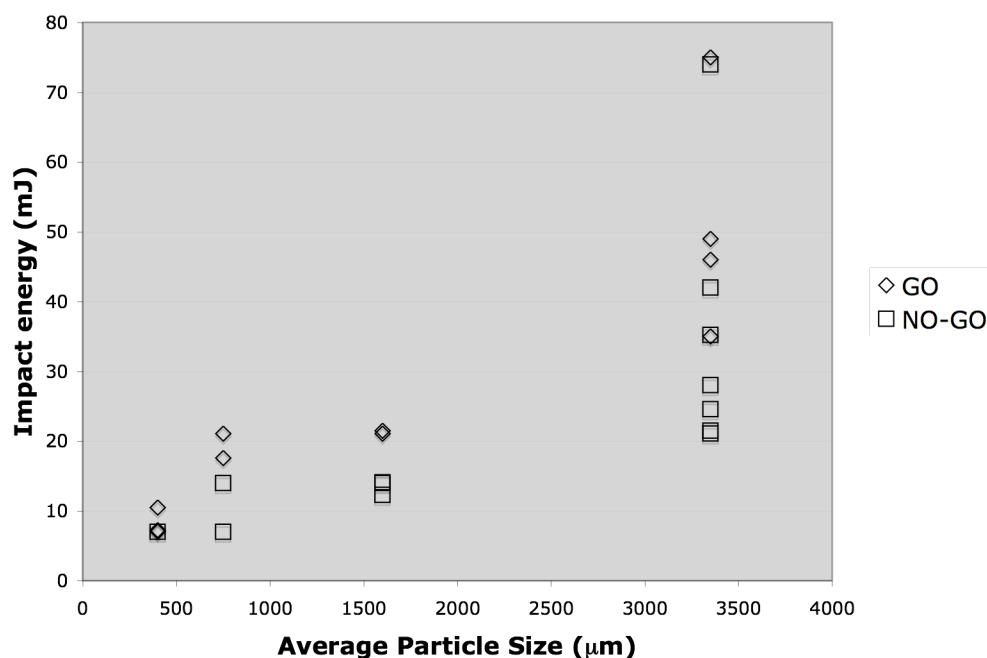
Figure 11. Plot of impact energy versus average particle size for an uncoated Al/Monel 400 multilayer material with a 20 nm bi-layer period, an overall thickness of 55 μm, and tested in configuration B (see Scheme 2 for clarification).

Figure 11 reveals and important and clear trend: That as particle size decreases so does the impact energy needed for stab initiation. These results are extremely relevant to this study as the ignition threshold for the mock detonators with the 400 μm, 750 μm, and 1600 μm average particle sizes have reproducible impact energies in the 5-20 mJ region. This is within the required region for stab detonators (3.5-35 mJ). Although subtle it is apparent that the threshold impact energies are consistently lower for the smallest average particle sizes tested.   For reference it should be noted that the largest particle size used were 3350 μm, which are ~ 0.125 " discs.

This trend was also observed for discrete particle sized materials that were fired in configuration D (see scheme2) powder only. This is reflected in the data shown below in Figure 12. Although there is some minor scatter in the data the trend line indicates that as the particle size of the energetic nanolaminate load decreases the sensitivity of the test device towards ignition increases. The impact sensitivities spanned by this data is wide. For example reliable and reproducible ignition was observed for impact energies as low as 5 mJ for devices containing energetic nanolaminate particles with an average size of 400 microns. Alternatively the sensitivity of test devices with 3350 μm disks of energetic nanolaminate showed reliable ignition above 45 mJ of impact energy, approximately an order of magnitude larger. This demonstration makes engineered energetic nanolaminate materials enabling for a wide range of mechanically initiated energetic systems.
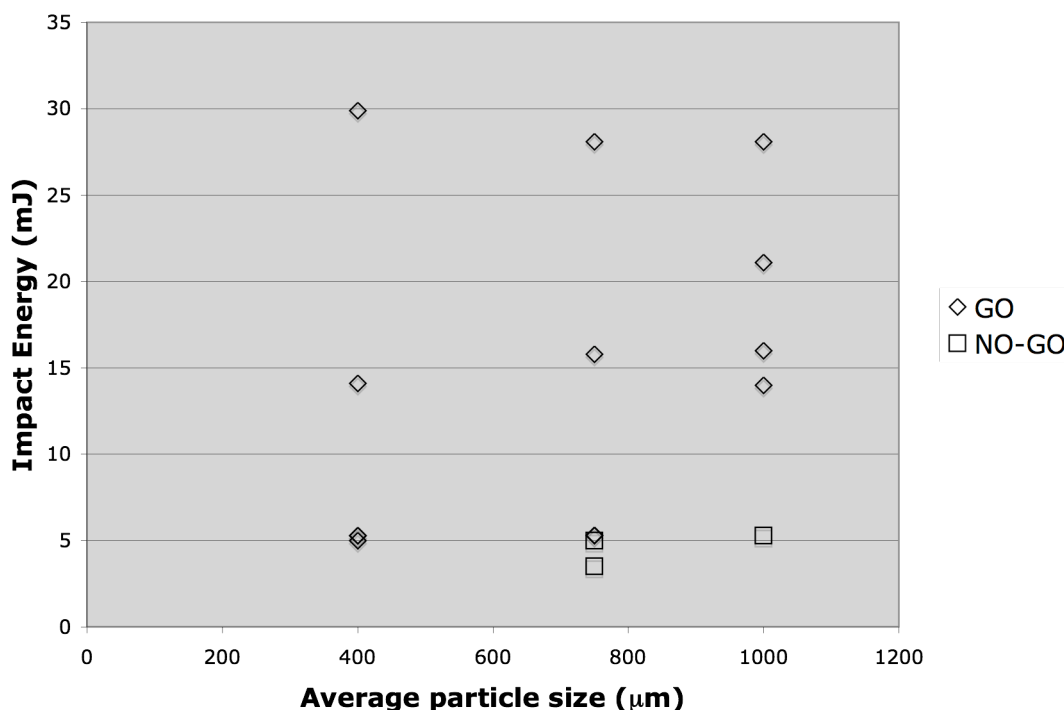
Figure 12. *Plot of impact energy vs. average particle size for un coated Al/Monel 400 multilayer particles with a thickness of 55 μm and a bilayer period of 20 nm for mock M55 stab detonators where the configuration was powder only (configuration D in Scheme 2).*

There are a number of potential reasons that the reduction in particle size leads to enhanced stab sensitivity of energetic nanolaminates. The compacted powder is less dense than a stack of macroscopic foils. Therefore it is more easily pierced through by the firing pin and thus get the more of the full effect of the tip/particle and interpartical frictional forces than a stack of disks. With a powder the frictional forces are enhanced relative to stacked monoliths.

Friction between surfaces is due to a combination of adhesion and plastic deformation. Adhesion can only occur at regions of contact and plastic deformation is caused by grooving, cracking, or ploughing of rough surfaces or edges. In the powdered energetic nanolaminate these interactions should be enhanced as the particle size decreases, which likely leads to the observed increase in stab sensitivity. Another possible reason for the increase in sensitivity is increased impacter tip/nanolaminate edge interactions with the powdered material. It has been previously reported that energetic nanolaminates were more easily initiated by impacts on the edge of the foil rather than in the body of the foil.[18,25] An edge is more easily deformed than the center. By decreasing the particle size of the nanolaminate foil the number of edges that interact with the impacter pin are increased leading to more possible initiation sites.

Once it was demonstrated that powdered energetic nanolaminates had stab sensitivities in the desirable range further evaluation of the materials in the device. One important parameter in the evaluation of stab detonators is their probability of initiation at the required levels was initiated.
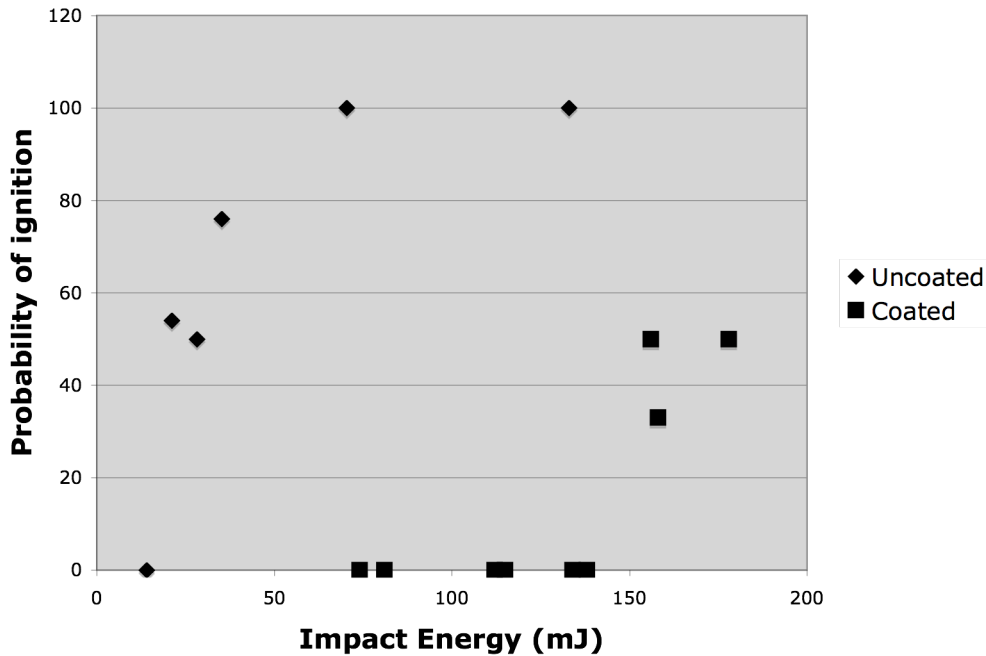
Figure 13. Probability of ignition of mock detonators using Al/Ni(V) energetic multilayer in configuration B. Each data point is derived from at least 5 and as many as 36 separate trials.

Figure 13 shows the relationship between probability of ignition and impact energy for two sets of Al/Ni(V) energetic multi-layers. Both of the materials have identical multilayer periods of 19 nm however the total thickness of the films are different 24 μm as compared to 9 μm and the 9 μm material has been over-coated with 800 nm of Al whereas the 24 μm material has no overcoat. This is reflected in the DSC data for each material that show the coated material has a total reaction energy about 20% lower than that of the uncoated.

Both sets of data show the same general behavior. The probability of initiation increases with increasing impact energy with an especially sharp increase in probability as the region of ignition threshold is approached and passed. The trend and position of each set of data in the figure is significant. The uncoated 24 μm thick material is readily initiated at comparatively lower impact energies indicating it is the more sensitive material in this configuration.

Table 2 contains a summary of the nanolaminate structural parameters as well as the minimum firing energy for each material evaluated in mock M55 testing in this project. From

Table 2. Summary of samples tested for stab sensitivity, their structural details and minimum stab energy needed for ignition. All stab energies shown here were for samples with a dis/powder/disk geometry (configuration B in scheme 2) and used powder retained on a W.S. Tyler Standard 50 Mesh sieve (particle size range is 300 μm to 500 μm)

Sample	Thickness (um)	Bi-layer Period (nm)	Coating	Min. Stab energy (mJ)
Al/Ni(V)-5	9	19	Yes	157
Al/Ni(V)-6	24	19	No	21
Al/Monel-3	25	18.2	No	18
Al/Monel-4	55	20.2	No	5
Al/Monel-5	26	62	Yes	>248
Al/Monel-6	12	25	Yes	>248
Al/Monel-7	13	10	Yes	>115
Al/Monel-9	23	16	Yes	99

this data it is apparent that the stab initiation energy can be engineered as there is a wide range of minimum firing energies. Values as low as 5 mJ and higher than ~250 mJ are observed. For clarification the highest impact energy tested was ~250 mJ. This data allows some quantification of the importance of each structural feature of an energetic nanolamiante to the minimum stab energy.   The influence of each structural feature in the stab initiation will now be discussed.

Coated Vs. uncoated

Without exception the coated materials display significantly higher minimum stab impact energies than uncoated foils. These results are consistent with the small-scale safety testing results from earlier in the report. Those results showed enhanced sensitivity of uncoated energetic nanolaminates on impact and friction testing relative to coated energetic nanolaminates. This is probably best illustrated in the minimum stab impact energy results from the entries for Al/Monel-9 and Al/Monel-3.   These samples have nearly the same total thicknesses (23 to 25 μm) and very similar bi-layer periods (16 to 18.2 nm), respectively. However their minimum impact energies to initiate were 99 mJ and 18 mJ, respectively. This trend is also observed when one compares the results from the Al/Ni(V)-5 and Al/Ni(V)-6. These materials have impact energies of 157 mJ and 21 mJ respectively. Both of the materials have identical multilayer periods of 19 nm however the total thickness of the films are different 24 um as compared to 9 μm and the 9 μm material has been over-coated with 800 nm of Al whereas the 24 μm material has no overcoat. This is reflected in the DSC data for each material that show the coated material has a total reaction energy about 20% lower than that of the uncoated.

The coating has the effect of desensitizing the energetic nanolaminate towards mechanical initiation.   One can postulate at least two reasons for this observation.   The overcoating of Al must act as an inert heat sink that adds no heat to the reaction wave that begins with heating from the localized mixing of the bi-layers induced by plastic deformation. The reaction only self propagates if heat is generated faster than it dissipates to the surroundings.

Alternatively, the overcoat layers may act to buffer the intermixing of adjacent layers from frictional interactions as the deformation of the surface layers do not result in exothermic output.

Total Thickness of foil

In general, the thicker the multilayer the more brittle it is. Thinner foils tend to be more flexible. A comparison of materials Al/Monel-3 and Al/Monel-4 are good example to illustrate any differences in sensitivity. The materials have identical composition very similar bi-layer periods but total thicknesses of 25 μm and 55 μm, respectively. The minimum stab energies for the two materials was 18 mJ and 5 mJ, respectively. With the thicker more brittle material more stab energy goes into plastic deformation of the foil whereas the thinner material undergoes more elastic deformation. It is likely that the plastic deformation leads to greater and more rapid intermixing of adjacent layers of metal.

Bi-layer Period

Of all the structural parameters of an energetic multilayer none has been more studied than the bi-layer period of the thin film.**[3-9]** This parameter has been demonstrated to have strong influence over the total energy, propagation velocity, and thresholds for mechanical and electrical ignition. This is to be expected as the bi-layer thickness defines the average diffusion distance for individual atoms to intermix. The larger this distance is the greater the barrier to initiate self-propagation. These and similar observations are more sufficiently addressed earlier in this article. It appears that this trend is also observed for stab initiation. Comparing the minimum stab ignition energies for the samples Al/Monel-5 and Al/Monel-9 is instructive.

Both samples have the same composition, are coated, and have nominally the same overall thickness, 26 μm to 23 μm. Their bi-layer periods are quite different 62 nm compared to 16 nm, respectively. The sample with the 62 nm period was unable to be stab initiated at the highest input energy level tested (~250 mJ) whereas that with the 16 nm period was ignited at 99 mJ.

In summary the data in Table 2 is very instructive on the influence of various structural parameters of energetic nanolaminates towards stab ignition. The trends observed from the data in Table 2 now provide a good basis for materials design for a particular application. For example, for an M55 stab detonator that must function in the 21-35 mJ range, the data in Table 2 suggest fabricating a material with a relatively fine bi-layer period (~20-25 nm), a larger total thickness, and one without any coating layers. The Al/Monel-4 material meets these criteria. In addition, to structural properties, it was determined in the course of this study that the physical arrangement of the nanolaminate in the stab detonator affected its sensitivity.

Current stab initiating mix materials are fine powders. The proposed replacement materials energetic multilayers can be processed into a monolith or reduced to a powder. This fact allows a number of potential configurations of the stab mix within the stab detonator. It was observed that the configuration of the energetic nanolaminate material within the stab detonator is extremely important for initiation within acceptable energy limits. A number of configurations were utilized in mock testing at LLNL and TACOM-ARDEC and live testing at TACOM-ARDEC. Representative configurations from this testing are shown in Scheme 2 below.
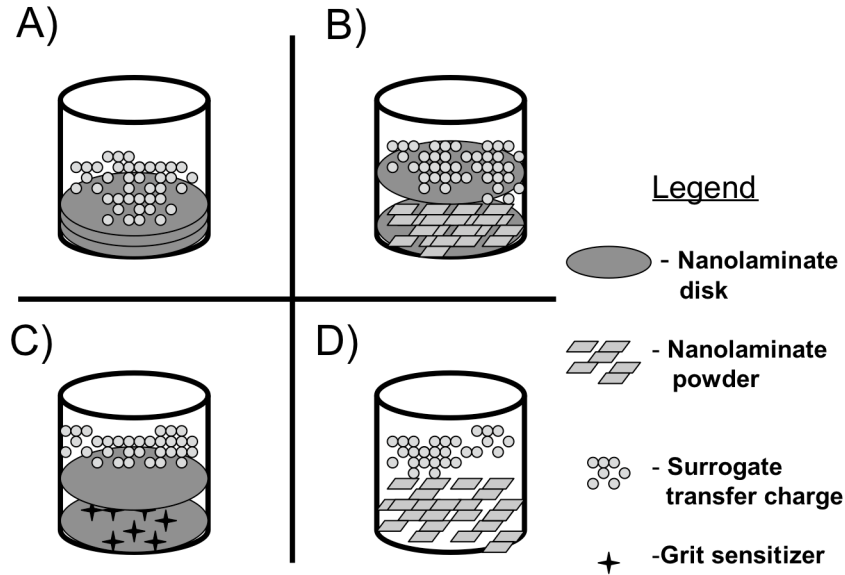
Scheme 2. Summary of important configurations utilized in stab detonator testing that integrated energetic nanolaminate disks and powders as the stab initiating mix. Notation used to describe each configuration in the text: a) Disk configuration, b) disk/powder/disk configuration, c) disk/abrasive/disk configuration, and d) powder configuration.

Results from the stab testing of mock M55 detonators demonstrate the importance of configuration on the minimum stab ignition energy. These results are summarized in Table 4.

Table 3. Influence of stab configuration on minimum stab energy for a 55 μm thick Al/Monel energetic multilayer system. The powder utilized in selected configurations was retained by W.S. Tyler Standard 35 mesh sieve.

Configuration	Minimum Stab Energy (mJ)
Powder	5
Disk/powder/disk	18
Disks w/Al$_2$O$_3$ grit	32
Disks w/o Grit	74

There is more than an order of magnitude difference in the minimum stab energy needed to ignite the stab mix. Minimum stab energies for the nanolaminates ranged from 5 mJ to 74 mJ for the different configurations with the highest being for the disks alone and the lowest for powder alone. The addition of a high melting point grit sensitizer (100 μm Al$_2$O$_3$) served to

lower the minimum stab energy for a configuration with only disks in it. This is a common practice and has been observed previously.**[25]** The small foreign particles have the effect of artificially introducing transient hot spots into the energetic material to sensitize it.

The data in Table 3 indicate that the incorporation of a coarse powder of energetic multilayer into the mock detonator drastically reduces the minimum firing energy of the mock device. There are several possible reasons for this. In all cases the firing pin must pierce the Al M55 cup, which dissipates some of the kinetic energy of the pin. However, in the case of configuration D (powder only) the remaining energy of the firing pin is transferred into the powder. In all of the other configurations the pin must pierce another barrier(s), namely the center of the disks of nanolaminate, and thus looses additional kinetic energy. Even though that energy goes into the energetic multilayer material the location of that energy transfer on the surface of the foil appears to be important. In fact, it has been previously reported that energetic nanolaminates were more easily and reproducibly initiated by impacts on the edge of the foil rather than in the body of the foil.**[25]**

Sensitization of stab detonators by mechanical means. Before the encouraging results with the powderized multilayers there was an effort to sensitize the multilayers using mechanical means. Specifically, the use of abrasive grit material and the use of hard and or meshed materials mixed in the initiating stab mix.

Traditional energetic materials can be enhanced with the addition of chemical or physical sensitizers. Examples of physical sensitizers are powders that have high hardness and high melting points. Typically the best results are obtained with materials with melting points above 550°C and fairly coarse (50-200 μm) particle sizes.**[26,27]** The small foreign particles have the effect of artificially introducing transient hot spots into the energetic material to sensitize it. It is highly possible that physical sensitization of these energetic multilayers is possible. It might also be possible to sensitize the multilayers by incorporating a wire mesh or hard anvil like material into the stab mix. These structures could provide areas of pinching or shearing when a multilayer foil is impacted through it by the firing pin. A mesh would still provide access for the hot reacting surface to contact the transfer charge that would be on the other side of it. In addition a small hard metallic cross could be used to promote a pinching initiation mechanism in the multilayer while still providing a hot contact area zone for stab mix/transfer charge interface. Figure 14 contains photos of two mesh samples and one steel cross structure that were used in these physical sensitization experiments.

a) *b)* *c)*
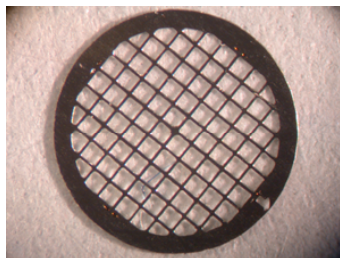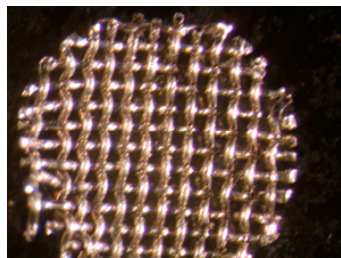
Figure 14. *Photos of mesh media a) and b) and cross (c) used to enhance pinching interactions with the energetic multilayer in stab detonator configurations. The diameter of each structure is nominally 3 mm.*

Limited experiments at ARDEC-TACOM indicated that the use of both types of meshes and the steel cross resulted in successful sensitization of the multilayer materials to an impact energy level of 5 in./oz. (35 mJ).

Sensitizing abrasive media was also used. Separate M55 mock detonators were prepared using aluminum oxide, silicon carbide, and ground glass, respectively. All of these materials were found to sensitize the stab detonators to acceptable levels. Once again these results are interesting, but given the important developments with the use of powders, there are no plans to continue to investigate the use of physical sensitizers in stab mixes containing energetic multilayers.

Timing of igntion and performance

Quite simply many explosive reactions result from highly localized heating which initiates a self-propagating reaction. In such a system one component in the system has its temperature raised which raises the temperature of the material adjacent to it, through some heat transfer pathway, to get that portion to react and further still. A rapid temperature rise of this nature can potentially lead to three types of reactions: thermal decomposition, deflagration, or explosion. The thermal initiation and explosion temperatures and time to reaction is known for a number of transfer charge and output charge explosives.[28] Therefore it would be useful to know the thermal evolution and time frame for that reaction in nanolamaintes initiated by stab. With that in mind experiments were done to determine the times to initiation, for maximum output, and total duration of the reaction, respectively.

For a number of reasons it may be necessary to utilize energetic nanolamainates as the first igniter in an ignition train. This could be due to cost, material, or space limitations. As demonstrated here the precision with which ignition thresholds can be tuned the energetic nanolamaintes are ideally suited to be the initial ignition point in a igniter or initiation train. In some instances it may be more cost effective to use a small amount of energetic nanolaminate. In other applications materials with alternative energetic characteristics may be needed to propagate the train. For example those with higher total energies and or materials that have different energy release characteristics (e.g, hot particle ejection, hot gas propagation) than are afforded from intermetallic thin foil reactions may be needed to ensure the inititation train propagates. With this in mind configurations of mock stab detonators were prepared and tested where thermite materials (both sol-gel and conventional) were either coated onto or pressed on top of energetic multilayer substrates in M55 mock detonator configurations. A series of still images from a high-speed video of one such test is shown in Figure 15a-g.
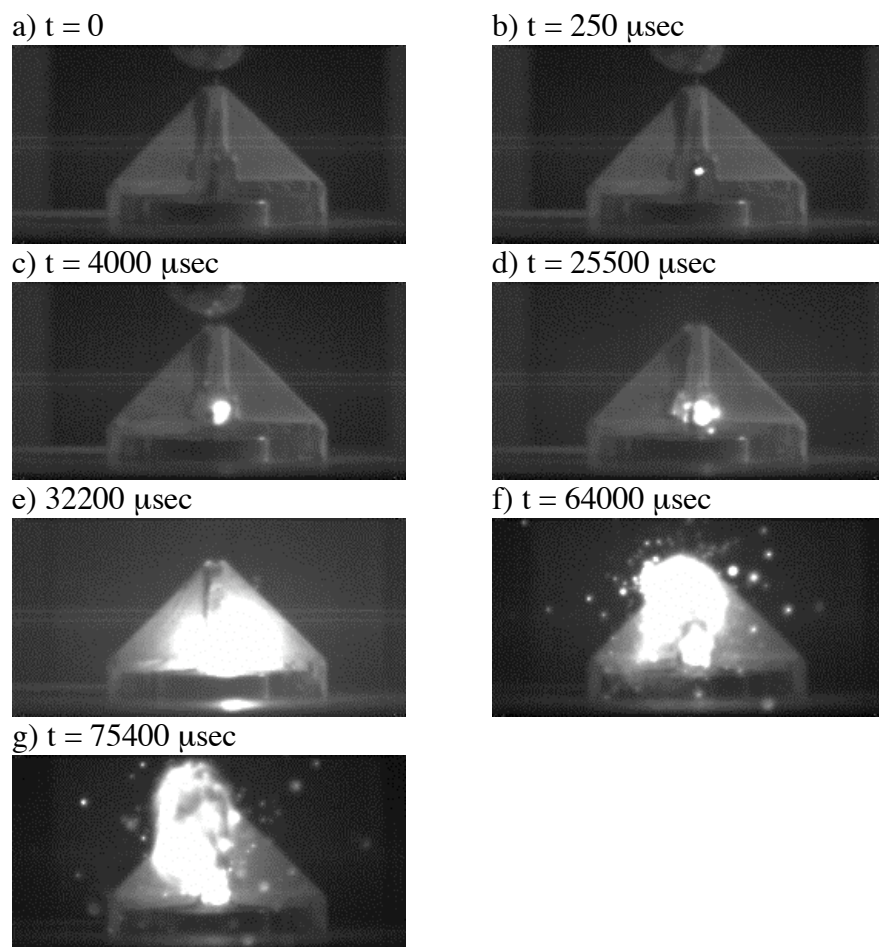
a) t = 0

b) t = 250 μsec

c) t = 4000 μsec

d) t = 25500 μsec

e) 32200 μsec

f) t = 64000 μsec

g) t = 75400 μsec

Figure 15. Series of photos from high-speed images of stab initiation of energetic multilayers and subsequently igniting thermite material.

Figure 15 contains a series of still images from high speed video taken of the stab initiation of a powder configuration of energetic nanolaminate that have had a powdered mixture of aluminum, iron (III) oxide, nickel, and Zonyl™ (fluoropolymer) pressed on top of it. The series of still images in Figure 15 capture the two-stage reaction of coated energetic nanolaminates. To allow the images to be captured the powder was packed into the end of a 4 mm diameter quartz tube. The image A in Figure 15 is a still of the very initial impact of the steel ball on the firing pin. The first visible sign of ignition was observed at 250 μsec in Figure 15 b. Once ignited the packed energetic multilayer powder self-propagates as is shown by the growing luminous plume in Figure 15c. The first visible sign of thermite ignition follows in Figure 14d at 25500 μsec. The secondary thermite reaction is observed to continue out to at least the 75000 μsec time frame. Visible hot particle ejection and a gas plume generated from the decomposition of the fluoropolymer characterize the energy release captured in Figure 15f.

The work described here recognizes and demonstrates the ability to tailor the ignition threshold of energetic multilayers. Therefore these materials hold promise for use in stab detonators, primers, and igniters. However in all of these applications the energetic multilayer

must be capable of igniting of initiating the next energetic material in the energy output train. The reacting multilayer undergoes solid-state combustion (gasless) and therefore energy transfer must be accomplished by thermal conduction or radiation. In many cases it would be desirable to transfer energy through the ejection of hot particles and gases. This desired effect can be accomplished by coating the energetic multilayer materials with thermite that is deposited by sol-gel processing or painting techniques. Here the energetic multilayer serves as the precision igniter and the energetic sol-gel functions as a low-cost, non-toxic, non-hazardous booster in the ignition train. Sol-gel thermite coatings like that shown in Figure 16 were deposited on energetic nanolaminate substrates with thicknesses from 2-100 μm.
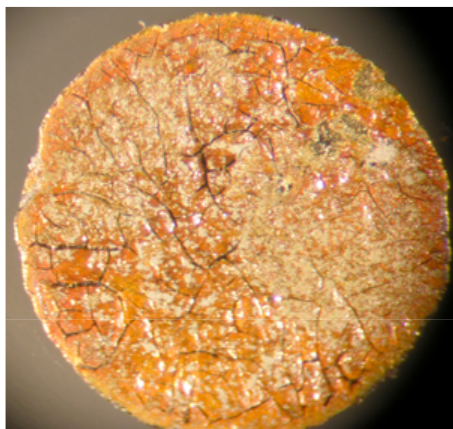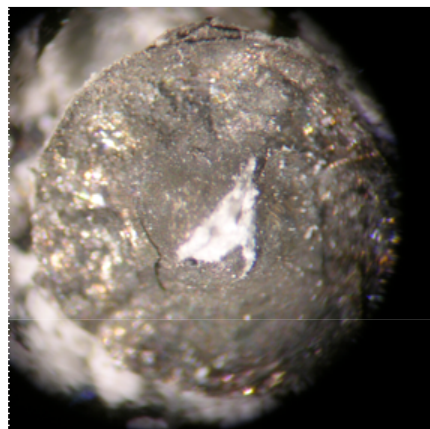
a)   *b)*

Figure 16. *Photos of sol-gel thermite-coated (Fe$_2$O$_3$/Al (2 μm) multilayer before a) and after b) stab initiation in the M55 mock detonator configuration.*

Using a configuration like this in the mock M55 detonator a coating of energetic sol gel thermite (Fe$_2$O$_3$/Al) can be initiated. Figure 16 shows photos of a disk of Al/Monel multilayer that has been coated with sol-gel thermite. There is a before photo and an after one Figure 16b. It is clear that the energetic thermite is reacted by the stab-initiated foil as is evidenced by the deposition of Fe metal particles (thermite reaction products) on the multilayer.

Reaction of the sol-gel thermite by a reacting foil was demonstrated in the M55 mock detonator testing as is shown in Figure 16 b. Being able to light the thermite is important for several reasons. It is more energy dense than the multilayer, which may aid in initiation of the detonation train (see technical approach section of this report). It is possible to incorporate gas generant in the sol-gel thermite layer (the multilayer is gasless), which may also aid in detonation train initiation. The sol-gel thermite is less expensive than the multilayer but is not stab sensitive, this provides a way to lower the cost of a new device while adhering to engineering requirements.

Further investigation of the energy release properties of the thermite coated energetic multilayer material was performed using differential scanning calorimetry (DSC). Figure 17 is

an overlay of DSC traces of samples of Al/Ni(V), and Al/Ni(V) energetic nanolaminate coated with thermite heated at a rate of 200°C/min.
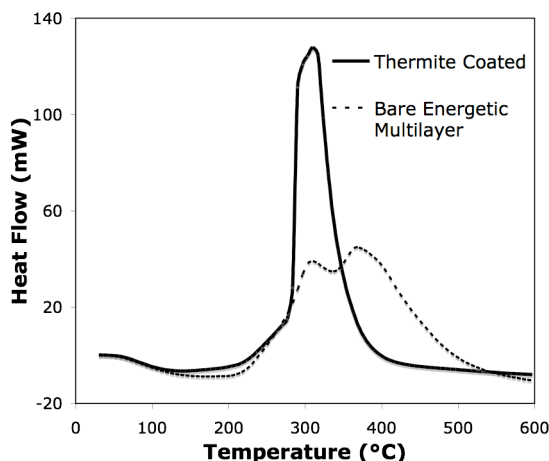

Figure 17. Differential scanning calorimetry traces for bare Al/Ni(V) multilayer and that coated with a thermite.

Although the total energy output of each material is similar the characteristics of that release are quite different. In the bare Al/Ni(V) multilayer the exothermic peak starts at roughly 210 °C has two distinctive and overlapping peaks and returns to baseline at ~500°C. Similarly the thermite-coated multilayer exothermic onset is identical to that of the bare multilayer, however the rest of the trace is quite different by comparison. The thermite-coated material has a single strongly exothermic peak that then returns to baseline at ~ 375°C. In addition the exotherm normally seen for the thermite at ~550°C is absent.

Clearly the rate of heat flow for the generated in each sample is quite different which indicates different kinetics for the two systems. On a basic level it is evident that, at the heating rate utilized in this experiment, the two energetic materials, multilayer substrate and thermite coating, energy release mechanisms become coupled. It is our belief that the rapid heating from the intermetallic reaction in the multilayer may provide localized heating to temperatures sufficient to ignite the thermite, which enhances the heat flow at the lower temperatures not seen in the bare Al/Ni(V) multilayer.

Although sol-gel coated nanolaminates were evaluated in mock detonator tests at LLNL and showed acceptable sensitivity the project terminated before the sol-gel coated materials could be evaluated in live detonators at Picatinny. Nonetheless live stab detonator testing was performed using neat energetic nanolaminate materials as the stab mix at Picatinny in the Spring of 2006.

Evaluation of Energetic Nanolaminates in Live M55 Detonators

Demonstration that reacting laminate will initiate lead azide. In the initial review of this proposed work reviewers raised concerns as to whether the reacting nanolaminate had the necessary energetic output to initiate the lead azide transfer charge material. This was addressed by revising the proposal to include a "go-no go" decision point task, which one aspect was demonstrating the efficacy of reacting nanolaminate to initiate lead azide. Experiments to address this were performed at TACOM-ARDEC. Aluminum/Monel 400 nanolaminates were used.
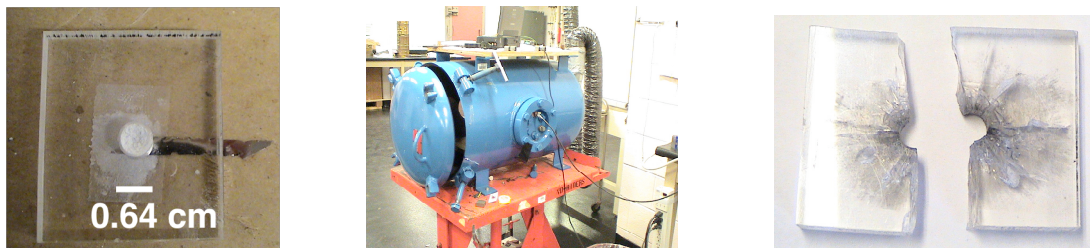

Figure 18. The photo on the top left is a Plexiglas plate with lead azide powder hand tamped in a hole in the middle. At the bottom of the plate is a nanolaminate foil strip that was in contact with the lead azide. The experiment test setup was put in a detonation chamber at Picatinny, shown above in the middle photo. The nanolaminate was ignited using a Nichrome hot wire. The reacting nanolaminate resulted in the detonation of the lead azide and shattering of the Plexiglas plate shown in the photo to the left.

The results of the experiment shown in Figure 18 are definitive: reacting nanolaminate will initiate the detonation of lead azide. A similar experiment was performed with the nanolaminate piece inserted into a M55 detonator cup with lead azide hand tamped on top. This also resulted in detonation of the lead azide. These experiments demonstrated that reacting nanolaminate will initiate the transfer charge material. Ideally this will be demonstrated, fully integrated, in a M55 detonator that is with transfer and output charge pressed and the cup sealed. Currently, efforts are being directed to demonstrate this. This input energy value is important, as above 35 mJ the transfer charge itself is stab sensitive. Thus, in any integrated experiment with an input energy above that level it will be impossible to determine if the nanolaminate has initiated the lead azide or the alternative. Similar experiments were also performed that demonstrate that the nanolaminate will also initiate the compound diaminohexazido cyclotetraphosphazene (DAHA). DAHA is a compound that has been considered as a non-toxic replacement for lead azide in the transfer charge of stab detonators.

Green detonator testing

Lead-free M55 stab detonators were formulated, fabricated, and tested at TACOM-ARDEC. The compositions of the respective components of the detonators were as follows: 1) the stab mix portion consisted of 55 μm thick Al/Monel 400 nanolaminate assembled in the disk/powder (300-500μm)/disk configuration (See Scheme 2) 2) the transfer charge was cyanuric

triazide and finally 3) the output charge was the TACOM-ARDEC formulation EDF-2C, which is a CL-20-based formulation. The lead-free M55 detonators were then tested on the drop weight apparatus at Picatinny. Lead witness plates were put under the detonators to quantify their energy output by post detonation analysis of the dent. Qualitatively, detonations were observed using the lead-free M55 detonators at drop heights of 3 in./oz. (21 mJ) and 5 in./oz. (35 mJ), respectively. For comparison a set of control tests were done with M55 detonators that were identical in composition to the lead-free ones except that 15 mg of the stab mix NOL-130 was utilized. Figure 19 contains photos of the lead witness plates from a test of

a)

b)

Figure 19. Photos of two representative lead witness plates from live M55 detonator testing at TACOM-ARDEC. The photo on the left a) is the dent left by an M55 stab detonator with an energetic nanolaminate stab mix/cyanuric triazide transfer charge and an output charge of EDF-2C. The one on the right b) is that left by an identical M55 stab detonator however with NOL-130 as the stab initiation mix.

of each type of detonator. By visual inspection the dents in Figure 19a-b appear to be very similar in diameter, depth, and total deformation of the plate. The dent from the M55 detonator with NOL-130 as the stab mix (Figure 19b) appears to be more symmetric than that from the lead-free M55 (Figure 19a). The maximum depth of the dent in Figure 19b was measured at 0.74 mm. The maximum depth of the dent in the plate in Figure 19a was measured at 0.76 mm (dent profile shown in Figure 20 below) and the width ~ 5 mm, Thus the two detonators had very similar results. It implies that the substitution of the current NOL-130 (lead-based) with a neat nanolaminate configuration did not affect the energy output of impact sensitivity of the device. In comparison with current M55 stab detonators (utilize NOL-130, lead azide transfer charge and RDX output charge,) both of these values are less than the typical observed dent depth value of ~2 mm.
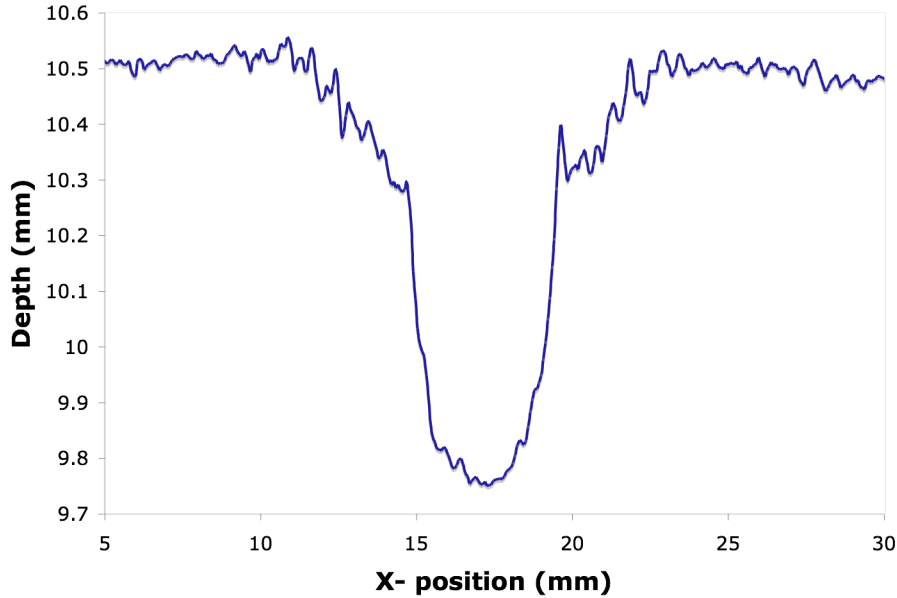
Figure 20. Trace of the dent profile in a lead witness plate from the testing of a lead free green M55 stab detonator fired at an impact energy of 21 mJ (3 in. oz.).

Conclusions

The goal of this work was to examine the efficacy of replacing lead-containing components of stab detonators used in medium caliber munitions using nanostructured energetic materials. More specifically, bimetallic energetic nanolaminate foils were applied to replace the stab mix component of stab detonators, which contains lead azide, lead azide, barium nitrate, antimony sulfide, and tetrazene. In this work the stab sensitivity of the energetic nanolamaintes were engineered to the required levels for M55 stab detonators. The influence of a number of nanostructural features of the laminate were shown to be critical to adjusting the stab sensitivity levels. These include the presence of coating layers, the bi-layer period, and the total thickness of the foil. In addition the form and physical arrangement of the nanolaminate strongly affects the stab sensitivity. Suitably engineered nanolamaintes were then integrated into the current M55 stab detonator design and demonstrated to detonate transfer charges of lead azide (current transfer charge), and two transfer charge replacement materials, cyanuric triazide and DAHA. Following on lead-free live M55 detonators were prepared using energetic nanolaminates as the stab mix and their energy output tested. Dents made in lead witness plates by the lead-free stab detonators were not as deep as those generated by the current M55 devices.

This includes replacing the toxic and hazardous components of current stab detonators with a more acceptable alternative in terms of performance and cost as well as health and environmental safety. Ideally this could be achieved with a benign replacement material. Reviews of this project have expressed concern with the use of nickel in these replacement materials. Nickel has health and environmental concerns of its own and its inclusion in new

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materials may become problematic. Currently, Ni or Ni-based alloy (Monel ($Cu_{0.3}Ni_{0.7}$)) is utilized in the many of the candidate nanolaminates. However undesirable, this has been justified and necessary.

To achieve early success there was a focus on these materials. To understand the critical structural elements of the multilayers, while using the Ni-containing compositions, that affect stab sensitivity, in general was critical. With that understanding now realized, the fabrication of a third generation energetic multilayer structure, engineered with the structural elements that are critical for stab sensitivity and whose composition is zirconium and aluminum, This composition was chosen while considering important factors such as cost, availability, environmental and safety issues, in addition to the favorable energetic properties of its heat of alloying. The enthalpy of reaction of the alloying of zirconium and aluminum is 1.18 J/g and the adiabatic temperature is 1650 °C. Further comment is warranted on the prospects for availability of energetic nanolamainte.

Energetic multilayers are currently commercially avaliable. One company, RNT Foil of Hunt Valley, MD makes energetic multilayers via this process for commercial applications.[10] Energetic multilayers are currently used for the microwelding of electronic components. With a supplier already in the marketplace these materials have the potential to be more than a curiosity pursued in an academic or national laboratory environment and are being considered for a number of applications involving energetic materials.

This work demonstrates the low energy stab ignition of several forms of energetic nanolaminate. Additionally the small-scale safety characteristics of energetic nanolaminates were evaluated for the first time. Important parameters that control stab ignition and the small-scale safety characteristics of these nanostrutctured energetic materials were identified. These characteristics include the total thickness of the multilayer, bi-layer period, the presence or absence of surface coating layers, and for stab ignition the physical arrangement and form of the energetic nanolaminates in the stab detonator. It was determined that coarse powders (400-600 μm) of energetic nanolaminate were up to an order of magnitude more sensitive to stab ignition than 2-3 millimeter sized diameter disks in mock M55 detonators. It was demonstrated that reacting energetic multilayers could be used to ignite other energetic materials such as thermite. All of these results illustrate the tunability of the ignition threshold and energy release characteristics of energetic nanolaminates. These aspects make these materials strong potential candidates for igniters, primers, and stab detonators with a broad range of energy input and output requirements.

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Appendices

List of Technical Publications

1. "Energetic Nano-Materials: Enhanced Energy, Engineered Energy Release and Initiation" Gash A.E.; Barbee, T.W., Jr.; Tringe, J. *Journal of Power and Propulsion* submitted April 2006.
2. "Mechanical Initiation of Energetic Nanolaminates", Gash, A.E.; Barbee, T.W., Jr. *manuscript in preparation for submission to Propellants Explosives and Pyrotechnics.*
3. "An Environmentally Robust Primer made with Nanotechnology" Barbee, T.W.; Gash, A.E.; Satcher, J.H., Jr.; Simpson, R.L. *Int. Annu. Conf of the ICT (34th ¹ Energetic Materials)*, Karlsruhe, Germany, June 24-27, 2003.
4. "Energetic Nanolaminates" Gash, A.E.; Barbee, T.W., Jr.; Tringe, J.*Progress in Astronautics and Aeronautics Series* Invited Book Chapter for 2007 publication.
5. "Stab Sensitivity of Energetic Multilayers" Gash, A.E.; Barbee, T.W., Jr. *Proceedings of the 33rd International Pyrotechnic Symposium*, **2006**, July 16-21 Ft. Collins, CO, USA.
6. **SERDP annual symposium abstract**

Other Technical Material

1. Nanolaminate-based Ignitors, Barbee, T.W., Jr., Simpson,R.L., Gash, A.E.; Satcher, J.H., Jr. patent filed September 2002.
2. "Methods for enhancing mechanical sensitivity of energetic multilayer initiation" Barbee, T.W., Jr., Gash, A.E Patent application filed May 18, **2006**