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# Environmentally Benign Stab Detonators

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*2005 Annual Report*

# Environmentally Benign Stab Detonators

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### *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.**[1]**

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%.**[1]** 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.

### *Objective*

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, iron

oxide and boron. These materials have much more desirable environmental and health characteristics than the NOL-130 composition.

***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 (A.K.A. flash metal) 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, and atomic layer epitaxy 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 vapor condenses 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. The sum of the thicknesses of two adjacent layers in the structure is referred to as the bi-layer thickness and is an important structural and performance parameter of the material. Figure 1 is a transmission electron micrograph of a multilayer structure with the bi-layer thickness outlined.

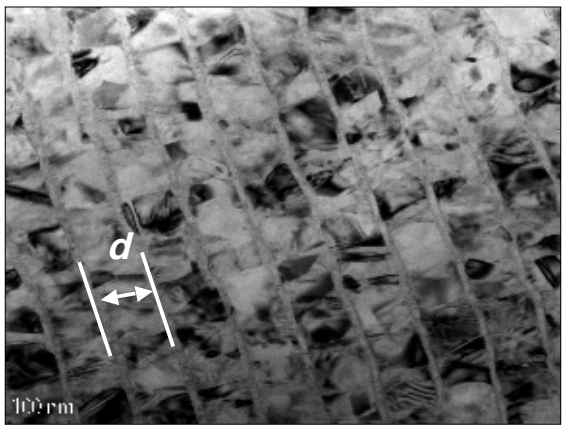



**Figure 1.** TEM image of a Zr/Cu nanolaminate thin film, the bi-layer thickness value is shown by the distance *d*.

One additional structural feature of energetic multilayer thin films not well illustrated by the image in Figure 1 is the so-called 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 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.

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.**[2,3]** The stored energy and reaction velocities of the

multilayers can be systematically and independently controlled by materials selection and size scale of the layers. 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. In addition, the method to prepare flash metals is affordable and the capital equipment and infrastructure currently exists in industry to do so.

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. **[2-5]**

*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.**[6-8]** 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.**[9-11]** 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.

*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 plan to focus on replacing the NOL-130 initiating mixture with a device that consists of a multilayer nanocomposite coated with a sol-gel energetic material. This material(s) will be prepared and physically characterized at LLNL and send to ARDEC-TACOM where testing on its performance characteristics will be carried out. Tests will include those for impact energy sensitivity. Feed back from ARDEC-TACOM will dictate the alteration of processing and compositional variables of the new IIDs at LLNL to alter the performance characteristics of the IID. Suitable candidate material(s) will be selected and ARDEC-TACOM will attempt 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 has changed this year. 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. 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.

### Summary of 2004 report and issues

To better express the progress in 2005 it is relevant to revisit the results and summary from 2004 on this project. While significant progress had been made in the areas of energetic multilayer fabrication, physical characterization, establishing safe handling and processing procedures, and stab sensitivity screening of candidate materials there was a critical challenge that had not yet been overcome. That challenge was the stab sensitivity of the candidate materials was not acceptable for M55 or M61 stab detonators. 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.

## Accomplishments

### Multilayer Fabrication

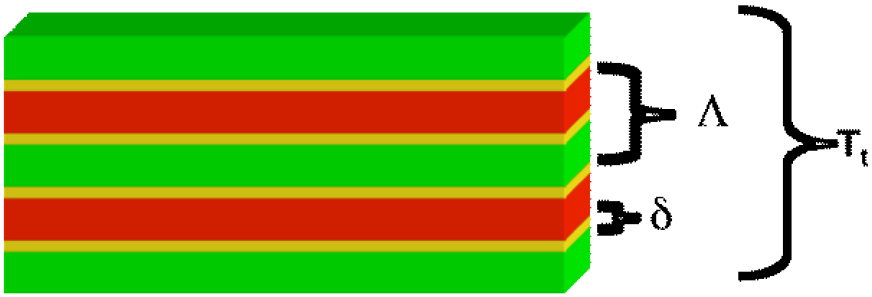
*Preparation of energetic multilayers with varied structure to enhance mechanical sensitivity*. Of specific interest to this project are the structural parameters of the nanolaminate and how they affect sensitivity and energy output of the device. Qualitative reasoning suggests that by decreasing the thickness of individual layers in the nanolaminate the reaction speed and sensitivity of the material would increase. The rationale for this is with decreasing bi-layer thickness (see Figure 1) the average diffusion distance between reactant species in adjacent layers decreases. A more detailed understanding of this reasoning is needed. The bi-layer thicknesses of the foils can be

readily and precisely controlled via magnetron sputtering. Therefore a series of nanolaminates with varied structure and composition were prepared at LLNL for this project. A summary of the energetic nanolaminates fabricated at LLNL is given in Table 1 below.

***Table 1.*** *Summary of structure of first generation energetic nanolaminates made and tested at LLNL.*

| Structure | | | | | |
|---|---|---|---|---|---|
| **Sample** | **Composition** | **# Top Layers** | **# Al/X Layers** | **Thickness** | **# Bottom Layers** |
| 294-TA21 | Al/Monel 400 | 10 | 1175 | 20 nm Al-13 nm Monel | 10 |
| 294-TA9 | Al/Monel 400 | 5 | 750 | 36 nm Al-12 nm Monel | 5 |
| 294-TA46 | Al/Monel 400 | 12 | 1432 | 10 nm Al-7 nm Monel | 12 |
| 294-TA16 | Al/Ti | 5 | 555 | NA | 5 |
| 294-TA35 | Zr/2Al | 2 | 1000 | 26 nm Al-18 nm Zr | 2 |

Through stab sensitivity testing, reported in the 2004 report and reconfirmed in 2005, it was determined that none of the multilayers in Table 1 were not suitably sensitive enough for use in M55 stab detonators. Therefore a need exists to enhance the mechanical sensitivity of energetic multilayers. It has been demonstrated that the total energy, initiation threshold, and burn rate of multilayers can be tailored by modification of their underlying microstructure.




***Scheme 1.*** *Scheme showing the structural features and terms 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

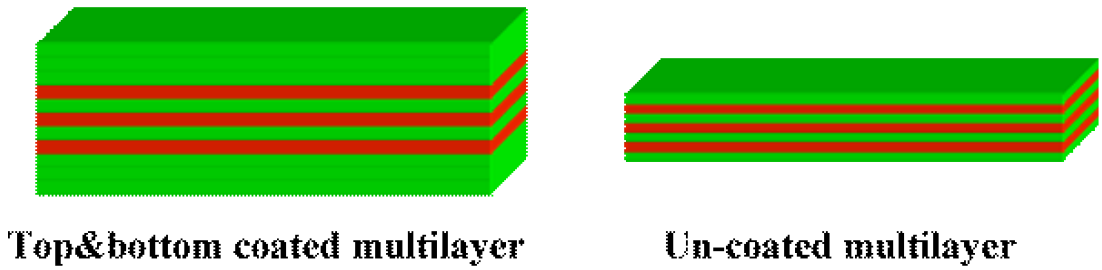
portion of Scheme 1. The distance corresponding to individual component layer thickness is set off by the small brackets in Scheme 1. The term referred to as the period, $\Lambda$, of the material is the distance of the repeating sub unit structure that makes up the foil. For example, in Scheme 1 $\Lambda$ 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. These parameters are important as they directly relate to the sensitivity and total energy output of the synthesized foils.

***Table 2.*** *Updated summary of structural parameters of second-generation multilayer foils engineered for enhanced sensitivity. Materials newly fabricated in 2005 are highlighted in red text.*

| Material | # Top layers | # Al/X Layers | Al layer (nm) | X layer (nm) | Capping layers |
|---|---|---|---|---|---|
| **Al/Monel-3** | None | 1351 | 10.4 | 6.8 | 15 nm Cu |
| **Al/Monel-4** | None | 2700 | 10.2 | 8.2 | 15 nm Cu |
| **Al/Monel-5** | None | 2775 | 10.9 | 8.8 | 15 nm Cu |
| **Al/Ni(V)-1** | None | 1442 | 10.6 | 7.5 | None |
| **Al/Ni(V)-2** | None | 1442 | 9.9 | 7 | None |
| **Al/Ni(V)-3** | None | 1852 | 7.95 | 5.64 | None |
| **Al/Ni(V)-4** | None | 1260 | 11.1 | 7.9 | None |

Some of the materials summarized in Table 2 were prepared and reported on in the 2004 Annual Report for this project. However efforts on multilayer fabrication for this project have continued in 2005 and the new materials are reported in red ink in Table 2. All of the multilayers reported in Table 2 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 2 the repeating bi-layer thickness (see $\Lambda$ in Scheme 1 and the sum of individual layers in Tables 1 and 2) was reduced relative to previous

materials. Also the materials in Table 2 were not over-coated with a final finish of several metallic Al layers, as was done previously (see Table 1). Scheme 2 illustrates both coated and uncoated multilayers. With no protective overcoat these materials




**Scheme 2.** Schematic representation of "coated" and "un-coated" multilayer materials, as is described in this report.

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. The materials summarized in Table 2 were fabricated with an emphasis to minimize the thickness of the pre-reaction zone of adjacent layers. It has been shown that a large pre-reaction zone has adverse effects on the total energy and reaction velocity of Al/Monel multilayers.**[2,3]**.

*Preparation of energetic multilayer materials that do not contain Ni.* The composition of materials shown in Tables 1 and 2, is an important topic and relevant to the goals for this project. 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 materials may become problematic. Currently, Ni or Ni-based alloy (Monel) is utilized in the many of the candidate nanolaminates. However undesirable this has been justified and necessary.

Historically LLNL has the most knowledge and experience with energetic nanolaminates that contain Ni. Previously, it was necessary to utilize materials that we have the most knowledge of and experience with to achieve early success. 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, has been achieved in 2005.

This composition was chosen while considering important factors such as cost, 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, see Figure 2 for a differential scanning calorimetry scan showing exothermic nature of the system.

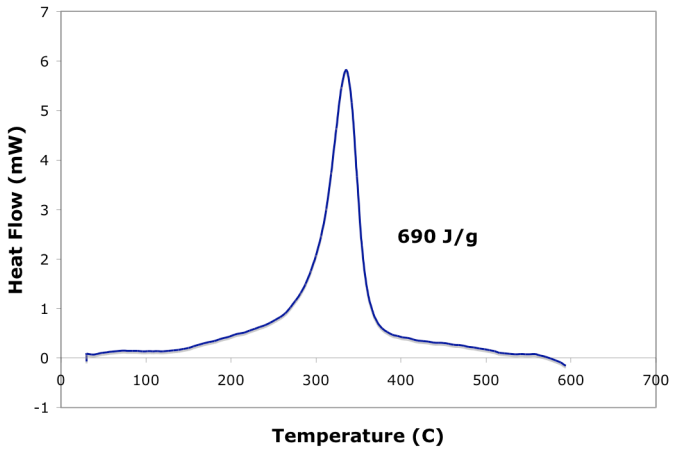



***Figure 2.*** *DSC trace of Zr/Al multilayer.*

This system is slightly less energetic than the Ni/Al system with an energy density of 1.38 J/g but has a slightly higher adiabatic reaction temperature than the Ni/Al system (1640 °C).

## Characterization of Energetic Multilayers

*Small-scale safety testing of newly fabricated energetic multilayers was revealing.* As was stated at the beginning of this section, the structural parameters engineered into these materials were done with the expressed goal of enhancing their sensitivity to impact and friction stimuli. Qualitative observations during handling of the materials in Table 2 indicate that this goal was achieved. The materials are more sensitive to ignition during handling processes such as cutting or punching of parts from the film. Nonetheless, films in Table 2 can be safely cut into smaller parts by following some general handling rules established. Punching and shearing of the material with precision shim punches at room temperature appears to be very effective for safe handling. However, it is imperative that the punches and shears be kept very clean. Ignitions tend to occur much more frequently when a punch has been used several times without cleaning.

Qualitatively these materials appear to be quite sensitive to lateral cutting action parallel to their layers that is typically introduced by scoring or scraping actions. This could be due to the absence of over-coating layers, which may allow mixing of adjacent reactant layers with relatively little mechanical input. To address this development in more quantitative terms we performed small-scale safety testing on selected materials.

Standard small-scale safety tests for explosives were performed on several energetic nanolaminates. These tests included the drop hammer test for impact sensitivity, the spark test for electrostatic sensitivity, and the B.A.M. friction test for friction sensitivity. **[14]** For reference the Drop Hammer at LLNL was calibrated with PETN, and RDX that have $DH_{50}$ values of 15.5 cm and 34.5 cm respectively and the B.A.M. friction ignites PETN one out of 10 trials (1/10) at 6.4 kg. Table 3 summarizes the standard small-scale safety test results for nanolaminate foils with specific structural features. This table has been updated from the 2004 report and new materials are highlighted in red text.

***Table 3.*** *Up-dated results of small-scale safety testing of selected energetic nanolaminates. Materials newly tested in 2005 are highlighted in red.*

| Material | *Foil (um)* | *d* (nm) | Al (nm) | Metal (nm) | Spark | B.A.M. Friction | Drop Hammer ($DH_{50}$-cm) |
|---|---|---|---|---|---|---|---|
| **Al/Monel** | | 26.7 | 15.8 | 10.9 | NA | NA | > 100* |
| **Al/Monel** | | 30.4 | 18 | 12.4 | 2/3 @ 0.04 J** | 1/10 @ 10.8 kg | 167.5 |
| **Al/Monel-3** | 24.7 | 18.2 | 11 | 7.2 | 2/2 @0.040 J | 1/10 @ 4.5 kg | 11.9 |
| **Al/Monel** | 23.3 | 17.2 | 10.4 | 6.8 | 2/2 @0.025 J* | NA | 18* |
| **Al/Monel-4** | 55 | 20.4 | 10.2 | 8.2 | 2/2 @0.040 J** | 1/10 @ 5.1 kg | 5.5 |
| **Al/Ni(V)-3a** | 24.3 | 18.1 | 10.6 | 7.5 | 2/2@ 0.04 J** | 1/10 @ 4.8 kg | 20.4 |
| **Al/Ni(V)-3b** | 26.2 | 16.9 | 9.9 | 7 | 2/2@ 0.04 J** | 1/10 @ 3.6 kg | 11.9 |
| **Al/Ni(V)-1** | | | | | 2/2@ 0.04 J** | 1/10 @ 4 kg | 13.0 |
| **Al/Ni(V)-2** | 25.2 | 13.6 | 7.95 | 5.64 | 2/2 @ 0.04 J** | 1/10 @ 3.4 kg | 14.3 |
| | | | | | | | |

**Tests performed at Picatinny (ARDEC-TACOM)*

***This is the lowest setting for the spark testing apparatus at LLNL*

There are several important conclusions that can be drawn from the data in Table 3. 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 material (compare structural parameters of the last three materials (shown in Table 1) in Table 3 to the first two (shown in Table 2). These are promising results as they indicate in a quantitative manner that the sensitivity of these energetic materials can be engineered. It is important to note that the influence of bi-layer thickness and over-coating layers does not appear to have the same drastic effect on spark sensitivity as it does on friction and impact sensitivity. Regardless of structure, all nanolaminates tested, via this method, here are very sensitive to spark discharge.

These results demonstrate, quantitatively, that the sensitivity of nanolaminates to mechanical impact can be tailored and controlled through control of its microstructure. It has yet to be determined whether this control is manifested through the bi-layer thickness, the pre-reaction thickness, or the extent of over-coating.

*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 is their aging characteristic. 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. Energetic multilayers are nanostructured, contain such fuel metals, and have high *interfacial* surface contact areas however their actual exposure to surface species such as gases is quite low. Previous generations of energetic nanolaminates have shown excellent stability on storing under ambient conditions up to 10 years, however these materials had capping layers to protect the underlying multilayer structure. As this effort has focused on enhancing the stab sensitivity of the materials through removal of these layers it is relevant to examine the stability of the uncoated energetic multilayers. Differential scanning calorimetry has demonstrated that this stability is good. Figure 3 contains the DSC scans of Al/Ni(V) multilayers from the same batch. In Figure 3a the sample was one month after fabrication and the scan in Figure 3b was after 14 months of storage under ambient conditions. One will note no difference in the total energy of the two foils indicating robust aging characteristics of the uncoated foil. This trend was also observed for the uncoated Al/Monel multilayers also (see Figure 4).

*a)* *b)*

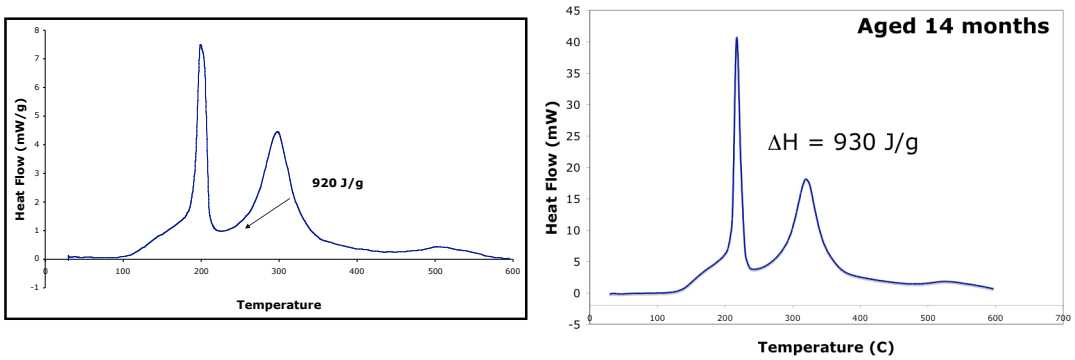



***Figure 3.*** *DSC traces for uncoated Al/Ni(V) films right after fabrication a) and after 14 months of storage under ambient conditions.*

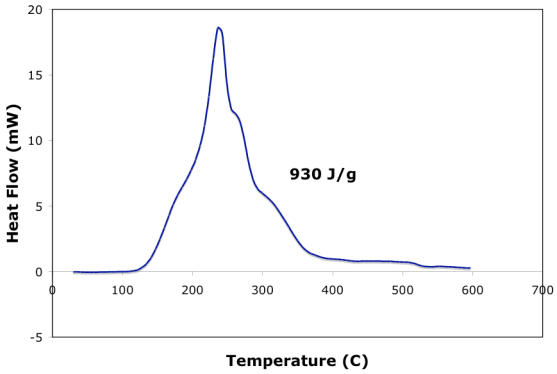
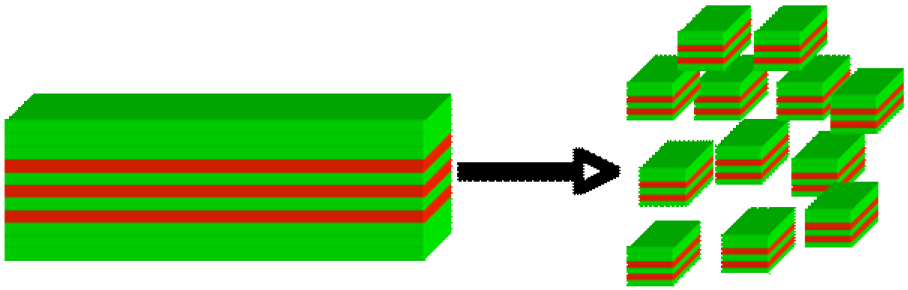



***Figure 4.*** *DSC of uncoated Al/Monel energetic multilayer 14 months after fabrication.*

## Processing of Energetic Multilayers

*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, see Scheme 3, and classification of that powder.

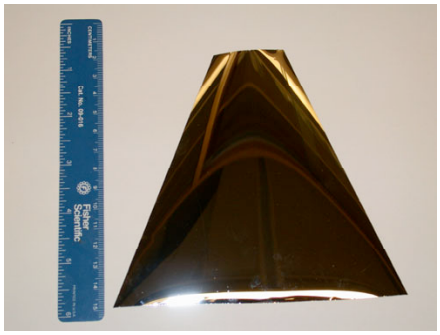


***Scheme 3.*** *Reduction of the energetic multilayer film to a "powder".*

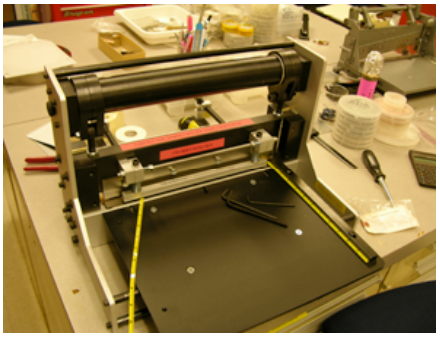
The term "powder" used in the rest of this report requires some defining as it is not a powder in the classic sense. Reducing the energetic multilayer to a "powder" essentially involves cutting and or shearing the sample into small square or rectangular pieces (with sub-millimeter dimensions) like that shown in Scheme 3. The pieces are still multilayers with large x and y dimensions relative to the foil thickness.

Up to this point the reduction of multilayer monoliths to powder and subsequent classification has been done essentially by hand. The process is summarized pictorially in Figures 5 and 6.

*a)*



*b)*



*c)*

*d)*

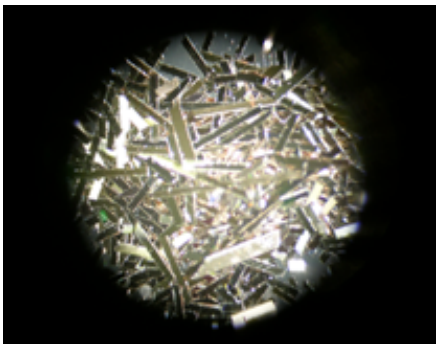


***Figure 5****. Photos summarizing the process of reduction of multilayer thin films to powdered material. Top left sheet a) is cut using the precision shear press b) into long fine thin strips of material (~2-10 cm long) which is then repeatedly passed through the shear press to produce an energetic multilayer powder d).*

In the process free standing foil pieces like that shown in Figure 5a are cut into long fine strips of material using a hand shear press like that shown in Figure 5b. The fine strips are then passed through the shear press several times to produce a powder of multilayer pieces. Using this process and equipment one person can produce 3-5 grams of powder in a day. Clearly the process described here would be problematic for any large-scale production of the material. However this process can be optimized a great deal.

*Methods being developed to scale-up and standardize the production of powdered multilayer material.* One approach being evaluated at LLNL is to pattern the energetic multilayer substrate to fracture along predetermined lines. Successful implementation of this will allow one to design a uniform powder with constant particle dimensions as well as improve the reduction to powder process and eliminate the need for the labor-intensive hand-shearing step. The goal of a standard and uniform particle size processing is a revised milestone for early 2006 and is under active investigation at LLNL.

Once a powder of energetic multilayers is produced from the process in Figure 5 it has a large number of dramatically 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 became very important. Through the use of standard stainless steel sieves a powder from the process is classified on the basis of particle size dimensions. Examples of the sieves and the fractions of particles that it yields are shown in Figure 6.

*a)*

*b)*

***Figure 6.*** *Photos of Tyler Standard sieves a) used to separate powdered multilayers into size-segregated fractions b).*

A number of different size fractions are separated and recovered and each is tested for its sensitivity to stab stimulus. Result from that testing will be discussed later in the report. A point of safety consideration here, no evidence has been observed to suggest that the energetic multilayer powders can be ignited through their agitation while sieving

**Testing of Energetic Multilayers in Mock Stab Detonator**

*New drop ball apparatus fabricated for improved reliability.* An important 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-weight 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.**[1]** 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).

A modified drop-weight test was used at LLNL for evaluating the qualitative stab sensitivity of nanolaminate films, as has been reported in the 2003 and 2004 reports. As more suitable candidate materials have been identified there has been a significant increase in the number of drop-ball tests performed as lower and more reproducible impact energies were desired. This increase in use exposed certain design flaws in the apparatus, especially in the area of reproducibility of the ball drop location. The head of the stab pin is quite small, thus the margin for error in the drop location was very small. To improve reliability of the test and productivity of the effort a new apparatus was designed and fabricated and is shown below in Figure 7.

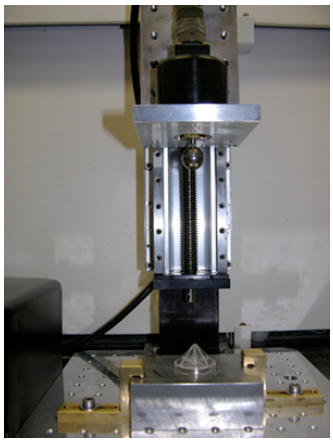
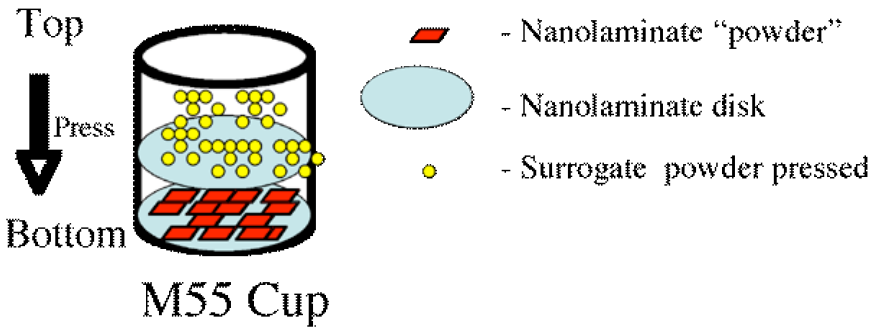


***Figure 7.*** Photo of newly designed and fabricated drop-ball apparatus at LLNL.

The new apparatus has two main improvements over the old one. First the drop mechanism is magnetic and ensures a clean and lateral displacement-free drop every time. Second the base plate and sample holder has been machined in place and are centered right under the release tip of the magnetic drop mechanism. These improvements have dramatically improved the reliability of the test apparatus and have improved the overall productivity of the effort.

*Desirable configuration of energetic multilayers determined.* Previous stab initiating mix materials have been fine powders. The proposed replacement materials energetic multilayers as has been demonstrated, can be processed as a monolith or reduced to a powder. This fact allows some variability in the design or configuration of the stab mix within the stab detonator. A desirable configuration has been determined and is summarized in Scheme 4.




***Scheme 4.*** Geometry of the "disk/powder/disk" configuration primarily used in this study. The M55 cup is aluminum and has a diameter of 3.3 mm

In this configuration one multilayer disk with a diameter of 3.17 mm is placed in the bottom of the M55 cup. The mass of one disk of this type is nominally ~2-3 mg. On top of that disk 6-8 mg of nanolaminate powder is poured and finally another disk is placed on top of the powder. This configuration is then tamped down in the cup, before the surrogate powder is pressed on top of it. Please note that the striker pin of the stab detonator pierces the bottom end of the M55 cup shown in Scheme 4 and therefore interact 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 $g/cm^3$).

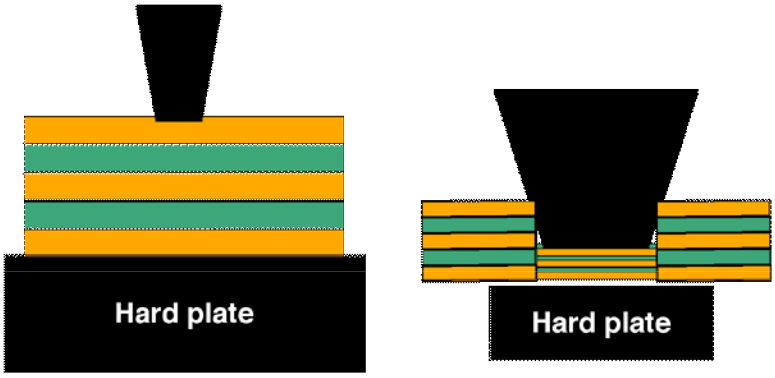
On top of the multilayer initiating portion of the device is where a surrogate powder is pressed (in the case of mock detonators) and where the transfer charge will be pressed in the case of live detonators. At LLNL both talc and lead chloride have been utilized as surrogate powders. At LLNL after loading of the surrogate material the powder was pressed at 500 psi and then an Al lid was crimped on to seal the device. At ARDEC-TACOM mock detonator tests using the same configuration were performed with talc as the surrogate transfer charge material.

Careful consideration and experimentation went into the design of this configuration and it has significant effects on the sensitivity of the mock detonators, as will be discussed shortly. The purpose of the initial disk is to provide a surface that when impacted first by the striker pin will impart a significant force across the area of multilayer powder. The uncoated powder particles have intra-particle void spaces that provide space for numerous powder particles to slide past one another where they have many opportunities to heat up of fracture or some combination of the two to ignite. Once ignited in a small portion the entire powder plug ignites. The top disk is then ignited and provides a large rapidly heated continuous hot surface to ensure heat shock initiation of the transfer charge (lead azide detonates above 370°C).

*Some comments on the mechanics and dynamics of stab initiation of energetic multilayer versus those of NOL-130 are in order.* It important to emphasize that the replacement material(s) will need to be initiated by a stab input. 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.**[15]** In that system it is 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 is theorized 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 particle 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 challenging as both the pin and energetic material have high thermal conductivities, 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

It is important to illustrate the difference between the mechanisms of initiation at work in the current system and those potential ones utilizing energetic multilayers. In the current IIDs, the mechanical energy of a metal conical striker driving through a tightly packed powdered energetic material is degraded to heat that initiates the powder starting the detonation train. Although the powder is tightly packed it still contains small void spaces, which may allow particle flow and heating that lead to initiation. In addition the packed stab mix has a much lower physical density (~ 3 g/cm$^3$) than for example a Ni(V)/Al multilayer with a density of 5.1 g/cm$^3$. Thus the powder takes much less mechanical energy to perforate with the pin. Previous iterations of stab tests with energetic multilayers there was no such powder. The "stab mix" was metallic foil disk(s) that are penetrated with a metal conical striker pin. There are significantly different mechanics between the two systems. There are limited previous studies on the mechanical sensitivity of energetic multilayers to self-propagating reactions.**[20]** None involve the mechanics that are present in the stab initiation scenario. Previously the mechanics used to initiate the reactive multilayers involved striking the foil with a hard impacter pin while it rested on a hard substrate (such as a metallic glass). It is very likely that in this and related experiments involved a pinching mechanism. With this mechanism the multilayer material is compressed between the two hard surfaces, the pin tip and the base plate. This compression likely leads to localized shear in the material during mechanical failure and heating in the multilayer, which enhances mixing of constituent layers and atoms, and subsequently leads to self-propagating reaction of the foil.




***Scheme 5.*** *Scheme of pinching mechanism of energetic multilayer foil initiation.*

It seems certain that the same mechanics are not occurring in stab detonators. More accurately the mechanics of the stab system can be summarized as they are in Scheme 5 with the caveat that the substrate is not hard. In fact by comparison, it is likely quite soft. Therefore it is unlikely that pinching of the metallic foil will occur without more significant modification of the components of the M55 or M61 detonator (this is addressed later in the report). This distinction must be made when considering future applications for these types of materials. For example for an application like percussion primers, where the percussion mix is crushed on top of an anvil, continuous multilayer parts may be particularly well suited as a pinching mechanism is likely at work.

*Enhanced sensitivity of energetic multilayer stab detonators.* A number of important experiments were run this year to try and enhance the stab sensitivity of mock M55 detonators that contained energetic multilayers in the initiating stab mix. The expressed goal was to sensitize the multilayer initiating mix to an acceptable level for the M55 that is reliable in the range of 0.5 in/oz. to 5.0 in./oz. (3.5 to 35 mJ) of impact energy. This was successfully accomplished using uncoated energetic multilayers in powder form both with and without the use of mechanical sensitizers. This is a very significant technical challenge that has now been overcome and should allow the rapid evaluation of live M55 detonators with multilayer stab mixes. It is the opinion of the author if this report that the future direction of this effort be centered on the production, characterization, and evaluation of stab detonators that utilize the powdered form of the multilayer without mechanical sensitizers.

*Mock Stab Detonator results from LLNL.* Using procedures described earlier in the report the stab sensitivity of several different uncoated 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 easy as the visual appearance of the materials after reacted is drastically different than before. Figures 8 and 9 illustrates this point well.

*a)* *b)*

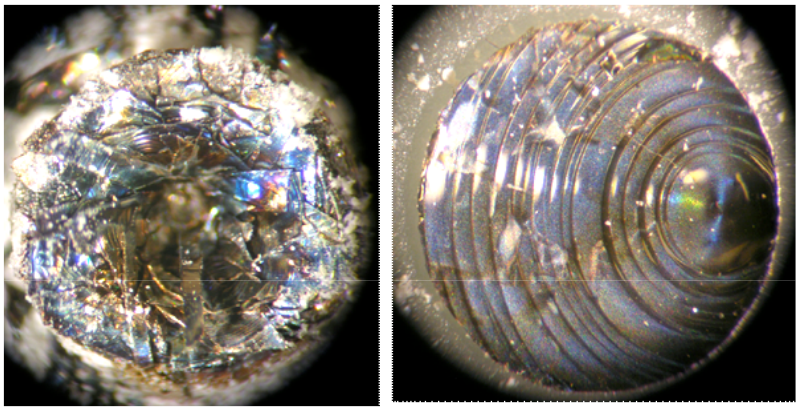


***Figure 8.*** *Photos of successful (go) reacted multilayer energetic foils materials. These materials were initiated in a M55 mock detonator configuration with stab input.*

Powder from the stabbed reacted foils tend to fuse together into one large plug that has been significantly deformed and is shown in Figure 8a. 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 unreacted multilayers is much different. This is well illustrated in Figure 9. The photo in Figure 9a shows a multilayer disk that has been perforated by a firing pin without reaction of the multilayer, and that in Figure 9b is that of unreacted powder. One can see that the material is still quite flat

*a)* *b)*

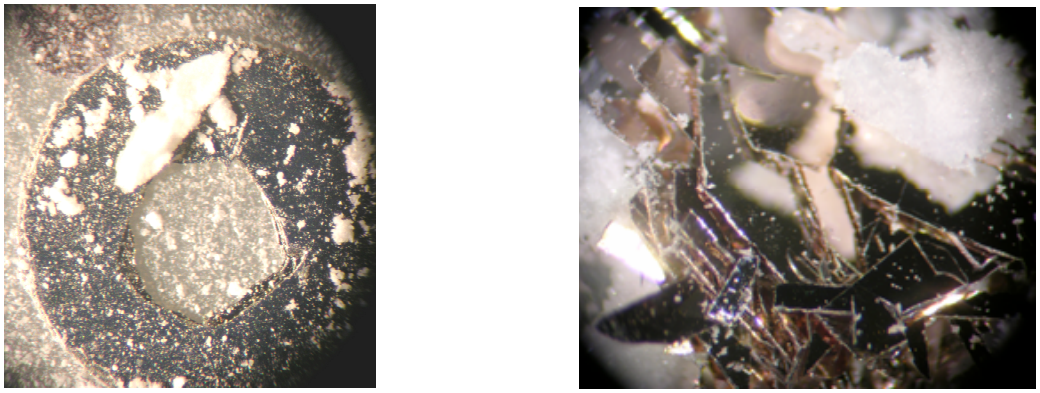


***Figure 9****. Photos of energetic multilayer disks a) and powder b) that has been stab impacted but that did not initiate.*

Previous mock stab detonator tests with 3 mm disks W.S. Tyler Standard sieve size 6 (3.3mm opening)) showed that impact energies above 70 mJ (10 in./oz) were needed to initiate the reaction. However the use of powdered multilayer material changes the stab sensitivity of the mock detonator dramatically as is illustrated in Figure 10.

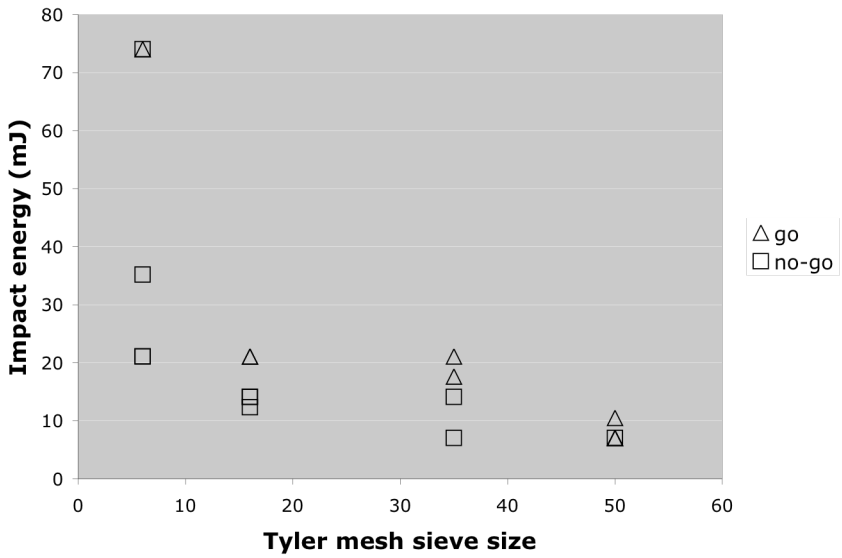



***Figure 10.*** *Plot of impact energy vs. Standard Tyler mesh sieve sizes for Al/Monel particles used in mock stab detonators. The configuration for these mock detonators was disk/powder/disk like that shown in Scheme 4.*

This plot shows that as the sieve size increases (e.g., particle size decreases) the impact energy needed for initiation decreases. This is extremely important as the ignition threshold for the Tyler Standard sieve sizes (No.s 18 (1.0 mm), 35 (0.5 mm), and 50 (0.297 mm)) are in the 5-20 mJ range. This is within the range required for stab detonators (3.5-35 mJ). It is also very interesting to note that there appears to be a trend that as the particle size decreases the impact energy tracks with it.

This trend is also observed in mock detonator configurations where only powdered multilayer was used with given particle size. These results are shown in Figure 11.

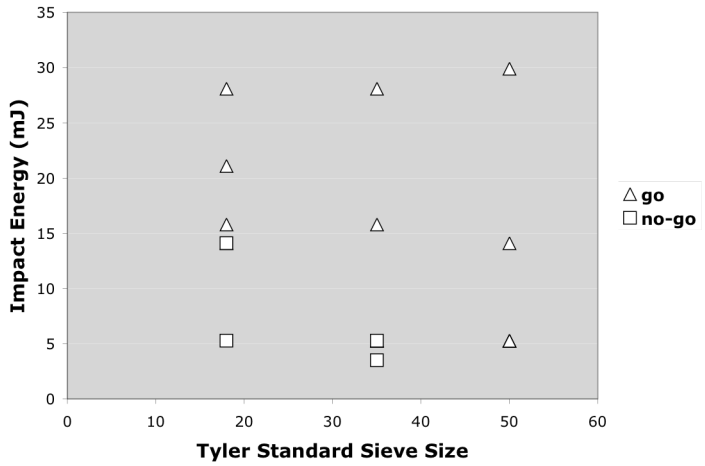



***Figure 11.*** *Plot of impact energy vs. Tyler standard sieve size for un coated Al/Monel multilayer particles for mock M55 stab detonators where the configuration was powder only.*

The sensitization of multilayers towards stab impact is not limited to the Al/monel system as it is observed in the Al/Ni (V) system also. This composition shows stab impact ignition in the 15-30 mJ range, which is also acceptable for current stab detonators.

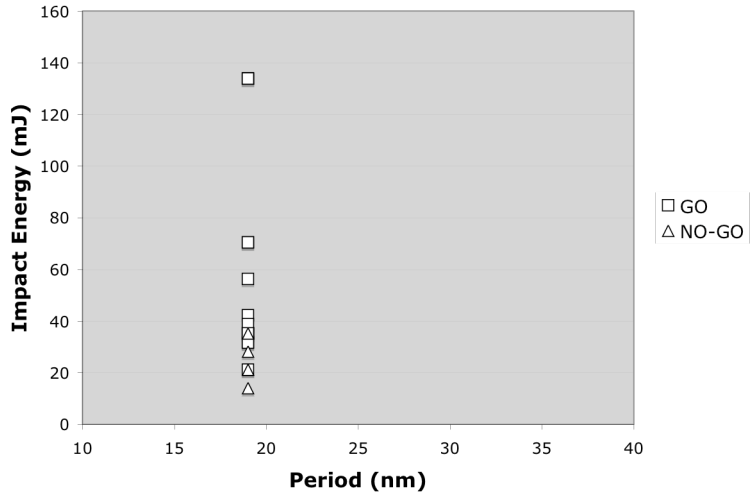



***Figure 12.*** *Plot of impact energy vs. multilayer period for uncoated Al/Ni(V) multilayer powders in the disk/powder/disk configuration.*

Finally the influence of coating layer on the multilayers and their sensitivity towards stab impact was evaluated with the results summarized in Figure 13 below.

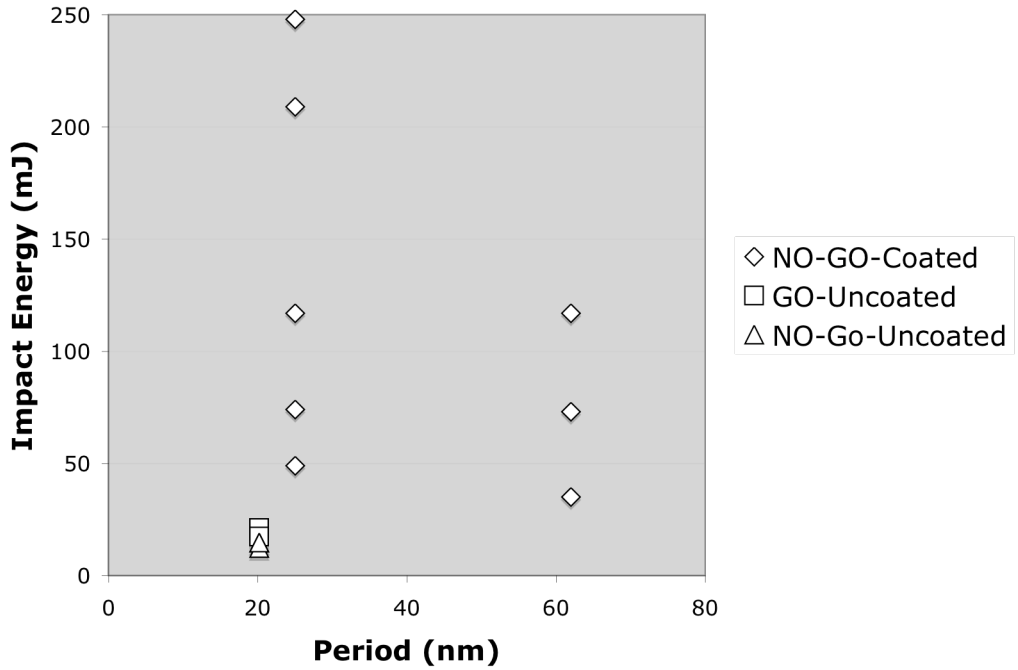



***Figure 13.*** *Plot of impact energy versus period structure for both coated and uncoated Al/Monel multilayer foils for M55 mock detonator tests in the disk/powder/disk configuration.*

It is evident that the uncoated foils have much lower impact energies than those of the coated multilayers. The results in Figure 13 suggest a strong correlation between the stab sensitivity of the materials and the presence of a coating on the multilayer. Although the period structure was finer for the uncoated materials ~20 nm relative to those for the coated materials (~25 nm, and ~63 nm) the coating may have a stronger effect on stab sensitivity as the difference between a period structure of 20 nm and 25nm does not seem that significant. That is it seems likely some impact sensitivity should have been seen for the 25 nm period case but none was up to the limit of testing (250 mJ). However at this point this is still conjecture. Appropriate experiments are planned to determine this effect with more certainty. Nonetheless, the qualitative observation that the coated materials are much less sensitive to initiation (even in the powdered form) than the uncoated ones is important to this project and its goals.

Using a configuration like this in the mock M55 detonator a coating of energetic sol gel thermite ($Fe_2O_3$/Al) can be initiated. Figure 14 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 14b. 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.

*a)* *b)*

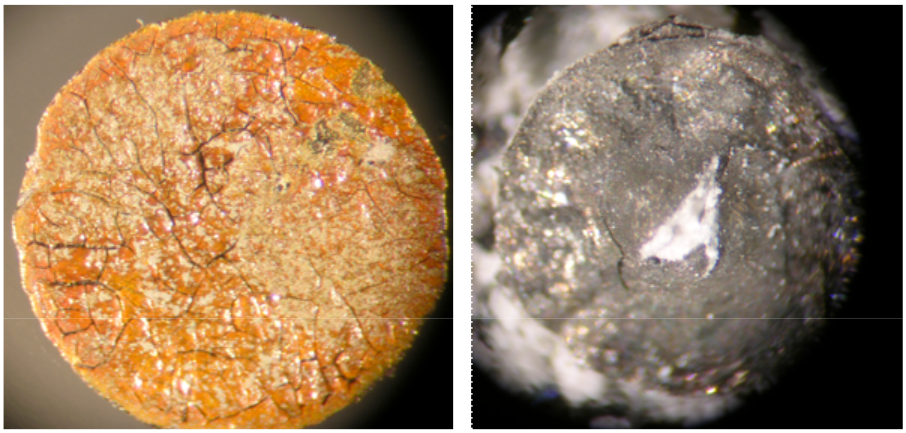


***Figure 14.*** *Photos of sol-gel thermite-coated multilayer before a) and after b) stab initiation in the M55 mock detonator configuration.*

Reaction of the sol-gel thermite by a reacting foil had been demonstrated already but not in the M55 mock detonator configuration. 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. 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.

*Mock stab detonator results from ARDEC*. After the demonstrated successful stab initiation of mock M55 detonators at LLNL it became important to transfer materials and the knowledge of the correct configuration to the Army collaborators at ARDEC-TACOM. The purpose of this was to confirm results from testing at LLNL and to give the Army an opportunity to gain more experience handling and formulating these materials in more of an application based environment.

Samples of four different energetic multilayer materials (two different Al/Monel and two different Al/Ni(V) materials) were sent and tested at ARDEC-TACOM. The multilayers sent were in the form of a mixed powder (not size segregated) and 3.2 mm disks. The Army tested the materials using the configuration shown in Scheme 3. A qualitative 'go' or 'no-go' result was determined by visual inspection of the mock detonator parts after drop testing. Testing results obtained by ARDEC-TACOM were consistent with those observed by LLNL. Nearly all samples loaded using the materials supplied by LLNL in the appropriate configuration were initiated on the Drop ball testing

apparatus at Picatinny at the 5 in./oz/ (35mJ), the upper limit for M55 stab detonators. Figure 15 is a photo of a stab initiated energetic multilayer from the Army's testing.

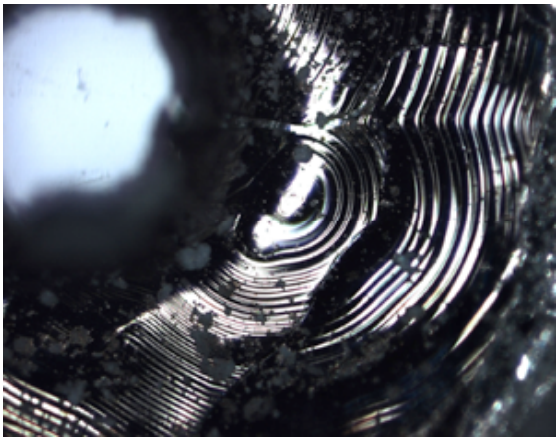


***Figure 15.*** *Photo of a stab initiated energetic multilayer tested at the Picatinny Arsenal.*

A second round of M55 mock detonator testing at impact energy of 3 in./oz. (21 mJ) also had a high rate of successful initiation.

It appears as if the stab sensitivity issue with the energetic multilayers has been overcome. This was done by modifying the structural features of the multilayer, utilizing a coarse powder of the multilayer, and using a desirable configuration. Both LLNL and ARDEC-TACOM have confirmed this result, which now allows the evaluation of energetic multilayers in live M55 detonators and comparison with the results for NOL-130. With that in mind work in early 2006 will focus on this. ARDEC-TACOM has agreed to prepare live M55 detonators with energetic multilayers as the stab mix and evaluate their energy output and performance characteristics (i.e., witness plate dent tests).

*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.**[16,17]** 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 16 contains photos of two mesh samples and one steel cross structure that were used in these physical sensitization experiments.

*a)* *b)* *c)*

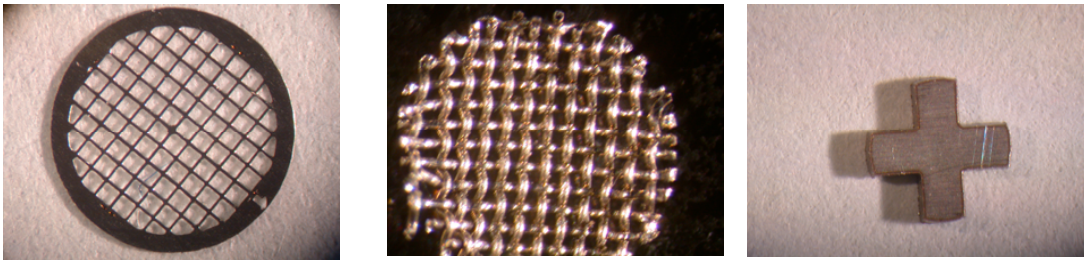


***Figure 16.*** *Photos of mesh media a) and b) and cross (c) used to enhance pinching interactions with the energetic multilayer in stab detonator configurations. The diameter of each structure is nominally 3 mm.*

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.

**Summary and Future Directions**

Progress on several fronts was made this year. As was mentioned throughout the report there was an emphasis on fabricating, characterizing, processing, and testing energetic multilayers with enhanced sensitivity for stab initiation. It was shown that the use of energetic multilayers as a coarse powder resulted in dramatic improvements in their stab sensitivities. The sensitivity level is now at acceptable levels for the M55 and M61 stab detonator. Both LLNL and the Army confirmed these results. This will enable

live detonator tests to be performed by the Army in the very near future results of which will be compared to existing stab detonators and allow a reasonable evaluation of the efficacy of green stab detonators.

It was determined that the sensitivity of the stab mix is increased as the particle size of the multilayer powder is decreased. Also the importance of uncoated multilayers to stab sensitivity was illustrated. Processing methods for converting monolithic energetic multilayers to coarse powder and size segregated them were demonstrated. Further improvements in the processing of multilayers to powders are the anticipated focus of work in the near future. In addition, multilayers, with appropriate structural features for stab sensitization, were fabricated that do not contain Ni were fabricated and will be characterized and tested in the new year. The concern there is to remove the toxic Ni from the solution for current stab detonators. Finally, it was demonstrated that physical sensitizers could be used to increase the sensitivity of multilayers to stab initiation. However, this approach to solving the stab detonator problem will not be pursued under this project.

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