



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Environmentally Benign Stab Detonators

A. Gash, T. Barbee, R. Simpson, J. Satcher, C.
Walton

December 29, 2003

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

FY03 Annual Report

Environmentally Benign Stab Detonators

PP-1362

Lawrence Livermore National Laboratory



PI: Dr. Alexander Gash
P.O. Box 808 L-092
Livermore, CA 94551
925-423-8618
gash2@llnl.gov

Contributors:
Dr. Troy Barbee
Dr. Randall Simpson
Dr. Joe Satcher
Dr. Chris Walton

Contents

	Page
Background	1
Objective	1
Technical Approach	2
<i>Nanolaminate materials and technology</i>	2
<i>Sol-gel energetic materials</i>	3
<i>Integration of the nanotechnologies</i>	4
<i>Interaction with Army and transition plans</i>	5
Accomplishments	5
<i>Quick-look at milestones</i>	5
<i>Fabrication of drop ball apparatus and screening of candidate materials</i> ...	6
<i>Synthesis and characterization of candidate nanolaminate foils</i>	8
<i>Processing of sheet nanolaminates into precise sizes and geometries</i>	12
<i>Fabrication and initial testing of sol-gel energetic coated nanolaminate</i> ...	13
Publications	16
Summary	16
References	16

List of Figures and Tables

Figure 1. Photo of drop ball apparatus fabricated at LLNL.....	7
Figure 2. Photo of sample holders and fire pins for M55 and M61 stab detonators...	8
Figure 3. Plot of period versus heat of reaction for Al/monel 400nanolaminates ...	10
Figure 4. Photo of a sheet of energetic nanolaminate.....	12
Figure 5. Photo of punched discs of energetic nanolaminates.....	13
Figure 6. Scheme of nanotechnology based IID.....	14
Figure 7. Mechanical initiation of a sol-gel coated energetic nanolaminate.....	15
Table 1. Summary of the milestones for this project.....	6
Table 2. Summary of important parameters for samples of Al/monel 400 laminate...	7
Table 3. Thermodynamics of selected intermetallic reactions	9
Table 4. Heat of reaction and product phases for Al/Zr nanolaminates.....	9

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 (lead azide), 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 reactive multilayer 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 ($\sim 2 \text{ \AA}$) to thousands of atoms thick ($>10,000 \text{ \AA}$). 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 its 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. Layers of different elements, each several nanometers thick, can be deposited on top of one another to make nanometer metallic multilayers. 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 shown to be sensitive to both thermal and mechanical stimulus.[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 μ m to 1000 μ m 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 substrate 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 Research Development and Engineering Center (ARDEC) at the Picatinny arsenal. The partnership with ARDEC 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 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) is being prepared and physically characterized at LLNL and send to ARDEC where testing on its performance characteristics will be carried out. Tests will include those for impact energy sensitivity. Feed back from ARDEC 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 will attempt to couple these initiating mixtures to lead azide transfer charge. Witness plate testing will be done at ARDEC on these new stab detonators according to specifications outlined in MIL-D-50865, MIL-D-14978, or MIL-D-70436. Once the new initiating mixture has been shown to provide the necessary energy output to transition the lead azide component, work will begin to find a suitable material to replace lead azide as the transition charge.

One promising candidate for the replacement of lead azide has already been identified in discussion with ARDEC. Upon anticipated selection of a suitable replacement for NOL-130, this device will be coupled with the candidate replacement charge material and the resulting IID will have its performance characterized. The 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.

Accomplishments

Quick-look at progress of planned milestones. We are pleased to report that three of the planned tasks for FY2003 have been started and are progressing nicely. A summary of the milestones for the entire planned 4-year project, their start, planned start, and estimated completion dates is shown below. As the remainder of this report will describe all three initial tasks slated for FY 2003 were started this year.

Table 1. Summary of milestones and their start and completion dates for this project.

Task	Started	Start	Completion	Status
Preparation of nanolaminate IIDs (LLNL)	Jun-03	NA	Dec-04	□
Physical characterization of nanolaminate IIDs (LLNL)	Jul-03	NA	Apr-05	□
Screening of Candidate IIDs	Sep-03	NA	Apr-05	□
Energy output & sensitivity characterization of candidate materials (ARDEC)	NA	Mar-04	Oct-04	□
Initiation of transfer charge (ARDEC)*	NA	May-04	Sep-04	□
Accelerated aging/performance studies (ARDEC)	NA	Nov-04	Jun-06	□
Alternative transfer charge development (LLNL/ARDEC)	NA	Dec-04	Dec-06	□

Status Legend	
Active task	□
Anticipate start in next 6 months	□
Anticipated start > 6 months	□

We have revised the completion date of one task, initiation of transfer charge (see the asterisk). This is a crucial task, and we are wary of rushing to start it without more progress on the other tasks. Completion of it will demonstrate that nanolaminate based IIDs can successfully initiate a lead azide transfer charge. This testing will be done at ARDEC. Initially we had planned for this task to be completed within 12 months of project start, with the current status of the project we anticipate it will be completed within 16 months of the start date, by September 2004.

Fabrication of Drop Ball Apparatus and initial screening of candidate materials. An important metric used in evaluating the efficacy of different materials as IIDs 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. 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. Percussion primers have higher firing energies, in the range of 18-60 in./oz. [1]

ARDEC has a drop ball apparatus for measuring impact energies, as well as significant experience operating it and interpreting the results from testing. We felt it

important that such a device also exist at LLNL. We intend to use the LLNL apparatus as a rapid screening test for certain materials and material combinations that show special promise in these applications. Candidate materials of interest will then be transitioned to ARDEC where they will integrate them into devices containing transfer charges and use their existing drop ball apparatus for more application driven characterization. This arrangement will allow the prudent allocation of resources needed for successful completion of the project.

With guidance from ARDEC we have fabricated a drop ball apparatus at LLNL to use as an “in house” evaluation of the sensitivity of these materials to mechanical stimuli. A photo of this apparatus is shown in Figure 1. ARDEC was very instrumental in accomplishing this with their technical advice as well as donation of firing pins and

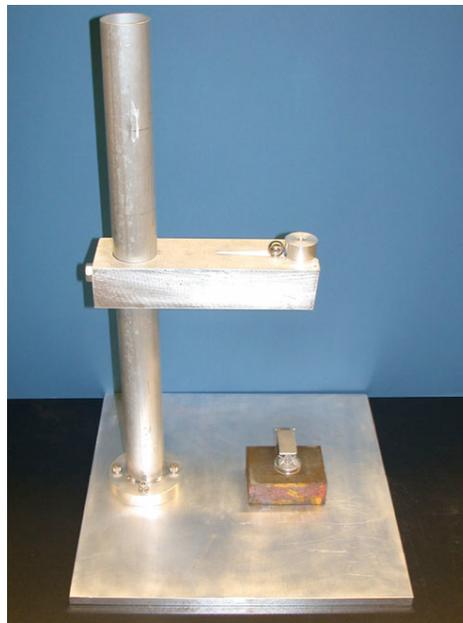


Figure 1. Photo of drop ball apparatus fabricated and in use at LLNL.

holders for M55 and M61 stab detonators. See Figure 2 for a photo of the holders and pins. Most stab initiators are similar in size and sensitivity and many use the same standard firing pin. These new devices would have to be integrated into the existing hardware for stab detonators therefore, it is critical that we use the current standard pins in our tests.



Figure 2. Photo of firing pins and sample holders used for testing of M55 (small pin) and M61 (large pin) stab detonators.

The apparatus at LLNL has gone through a few design modifications that make it slightly different than the one at ARDEC however the intent of the LLNL instrument as a screening tool is not diminished by them.

Using this apparatus we have characterized the sensitivity of nanolaminate materials. One material in particular has been identified as a promising candidate. That material is an Al/monel 400 nanolaminate. Monel 400 is an alloy of copper and nickel ($\text{Cu}_{0.3}\text{Ni}_{0.7}$). We have been able to impact initiate foils of this material at energies as low as 12 in./oz. This firing energy is greater than that of current stab detonators but less than that of percussion primers. Current IIDs initiate at impacts of ≈ 5 in./oz. It is most desirable for new candidate IIDs to initiate at energies similar to current ones. Therefore, we are attempting to engineer the sensitivity of the composition by varying the structural parameters of the nanolaminate. Engineered materials have been prepared and characterized (Table 1). These samples are currently being evaluated with the drop ball apparatus. We anticipate that from this set of materials nanolaminates with desired firing energies will be identified. When that is done larger amounts of material with the desired structural parameters will be fabricated, processed, and transitioned to ARDEC for testing in stab detonator configurations, including those with lead azide transfer charges. We expect that a material from Table 1 will be demonstrated to initiate the lead azide transfer charge in testing at ARDEC. This is an important milestone that we anticipate achieving by June 04.

Synthesis and characterization of candidate nanolaminate foils. With the identification of a promising candidate foil composition we have begun studying this particular material in greater detail. Of specific interest to this project are the synthesis and structural parameters of the nanolaminate and how they affect sensitivity and energy

output of the device. It has already been established qualitatively that by decreasing the thickness of individual layers in the nanolaminate the sensitivity of the material increases. However, we feel a more quantitative understanding of this and its relationship to thermal and energy output of the final material is important. For example, with detailed characterization and quantization of the thermal characteristics and energy output of the Al/monel 400 material we will be able to identify other, potentially more environmentally benign, candidate materials using these metrics.

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 Figure 6. The distance corresponding to individual component layer thickness is set off by the small brackets in Figure 6. Finally, the term referred to as the period, d , of the material is the distance of the repeating sub unit structure that makes up the foil. For example, in Figure 6 the period is the sum of the thicknesses of one Al and one Ni layer as together they make up the repeating substructure. These parameters are important as they directly relate to the sensitivity and total energy output of the synthesized foils.

To more fully deduce the effects of varying each of these parameters we have prepared and partially characterized a series of samples with varying overall thickness, period, and individual layer thickness. A summary of these material and parameters is shown in Table 1.

Table 1. Summary of foil thickness, period size, and individual component layer thicknesses for a series of samples of the nanolaminate material Al/monel400.

Overall foil Thickness (μm)	d (period) (\AA)	Al layer thickness (\AA)	Monel 400 layer thickness (\AA)
29.5	375	255	120
31	395	268	126
32	408	277	130
30	382	260	122
27.5	350	238	112
28.5	366	249	117
26	331	225	106
23.5	299	203	96
20	255	173	81
18	229	156	73
14	178	121	57
12	152	103	49

With this type of rigorous characterization we are beginning to understand the fine balance between period length and total energy output as is demonstrated in Figure 3 for Al/monel 400.

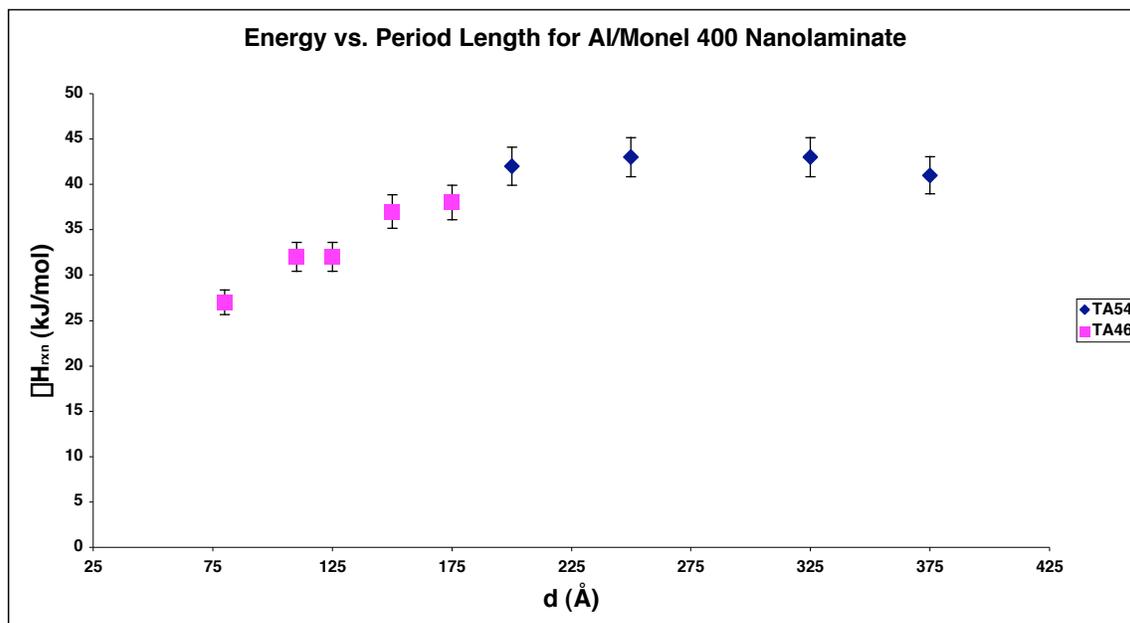


Figure 3. Plot of the relationship between period thickness and heat of reaction for two Al/monel 400 nanolaminate materials.

The data presented in Figure 3 is very important. It describes the critical structural point ($\sim 175\text{\AA}$ period length) where the overall energy output for the Al/monel 400 system begins to fall off. The decrease in measured ΔH_{rxn} (measured by DSC) occurs because as the individual layer thicknesses decrease (along with the period) the amount of pre-reacted material at the interfaces of layers increases. When this amount of pre-reacted materials rises to a substantial fraction of the volume of material it begins to affect the measured thermodynamic properties. This is important data because it gives us a limit, on a promising candidate material, for varying the nanostructure of the laminate, while maintaining the desired overall energy output.

Although one promising candidate material has been identified at LLNL we continue to investigate other compositions. Two nanolaminate compositions of particular interest to us are Al/Ti and Al/Zr. These are especially attractive as their components are considered to be safe and non-toxic and their energy output and thermal characteristics are similar to that of Al/monel 400. Several nano-laminate

aluminum/transition metal candidates have been investigated. Thermodynamic properties and calculated adiabatic reaction temperatures for aluminum/zirconium, aluminum/titanium and aluminum/nickel are presented in Table 1. The adiabatic temperatures are seen to be high.

Table 2. Thermodynamics of Selected Intermetallic Compound Formation Reactions

Reaction	Heat of Reaction (kJ per mole atoms)	Calculated Adiabatic Reaction Temp. (°C)	Reaction Product Phases
Zr + Al -> ZrAl	-45	1480	solid & liquid
Ti + Al -> TiAl	-36	1227	solid
Ni + Al -> NiAl	-59	1639	solid & liquid

We note here that measurements of the adiabatic reaction temperature for an Al-25.4 at% Zr yielded a value of 1400 °C ± 50. This is in reasonable agreement with the predicted value of 1480 °C as expected from the Differential Scanning Calorimeter data presented in Table 2. The total exothermic heat for the Al-25.4 at% Zr sample was 46.5 ± 3.5 kJ/mole atoms, being essentially equal to the value of 45 kJ/mole atoms used in the adiabatic temperature calculation. Though the Al/Zr system is very promising, the initiator work described here was done using Al/moনে1400 nano-laminates.

Table 3. Phases formed and total exothermic heat determined by Differential Scanning Calorimetry for Al/Zr nano-laminates as a function of increasing Zr concentration

Composition	Products of Reactions		ΔH_f
(atomic% Zr)	(Expected)	(Obtained)	(kJ/mol atoms)
7.6	Al & Al ₃ Zr	Al & Al ₃ Zr	16.6 ± 0.7
25.4	Al ₃ Zr & Al ₂ Zr	Al ₃ Zr & Al ₂ Zr	46.5 ± 3.5
30.5	Al ₃ Zr & Al ₂ Zr	Al ₃ Zr & Al ₂ Zr	51.4 ± 3.6
46.8	AlZr & Al ₃ Zr ₂	Al ₃ Zr ₂	52.1 ± 0.9
63.7	AlZr ₂ & Al ₃ Zr ₂	AlZr ₂	36.2 ± 3.2

As is well demonstrated in Table 3 we have a great deal of control over the energy output of these materials through manipulation of the reactant stoichiometries. With this control

we can tailor the energetic output of the IIDs, which will be important in many of their uses. This is advantageous, as in many current systems one would have to change materials to get such a variation in energy outputs. With this approach we keep the environmentally benign composition of reactants and products while changing the thermodynamics, as may be required by the initiation train.

Processing of sheet nanolaminates into precise sizes and geometries. An important concern for the application of these materials as IIDs is their processing characteristics. One particular concern we had was the cutting of nanolaminates into parts suitable for stab detonator testing. Nanolaminates are prepared as large sheets of material, see Figure 4. For integration into devices parts, with defined sizes and shapes must be cut out of the sheets. Cutting results in significant shear forces exerted on the energetic foil. Clearly we are concerned with being able to do this without igniting the foil.

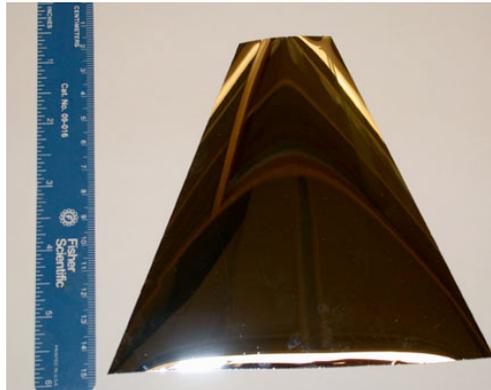


Figure 4. Photo of a sheet of energetic nanolaminate foil.

Up to now we have had considerable success in safely cutting energetic nanolaminates using a precision shim punch. Photos of some discs punched out of an Al/monel 400 nanolaminate are shown below in Figure 5.

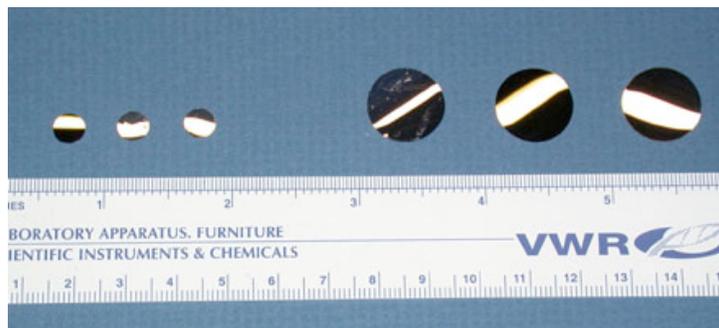


Figure 5. Photo of a punched discs of Al/monel 400 nanolaminate, small discs have a diameter of 0.64 cm and large discs are 1.60cm in diameter.

These materials are punched out at room temperature and we have not observed any unintended ignitions to this point. With more sensitive structures or compositions this may become a problem. If it does arise there are strategies to address it. One alternative is to cool the nanolaminate substrate to acceptable levels that will allow shear forces without generating a self-sustaining reaction. A second alternative, would be to deposit the nanolaminate on a textured substrate that is designed with the desired size and geometry of the parts. This should provide points and lines upon which the nanolaminate may be preferentially fractured into the desired shapes and sizes with little mechanical energy input.

Fabrication and initial testing of sol-gel energetic coated nanolaminate. We have successfully dip-coated Ni/Al flash metal multilayer foil with pyrotechnic-based sol-gel materials. Preliminary experiments have indicated that the conversion of a Ni/Al multilayer to its respective intermetallic generates sufficient energy to ignite the more energetic $\text{Fe}_2\text{O}_3/\text{Al}$ composite coating. An idealized scheme of what this material looks like on the microscale is shown in Figure 6. The $\text{Fe}_2\text{O}_3/\text{Al}$ nanocomposites ignite and burn at temperatures exceeding 3000 K.

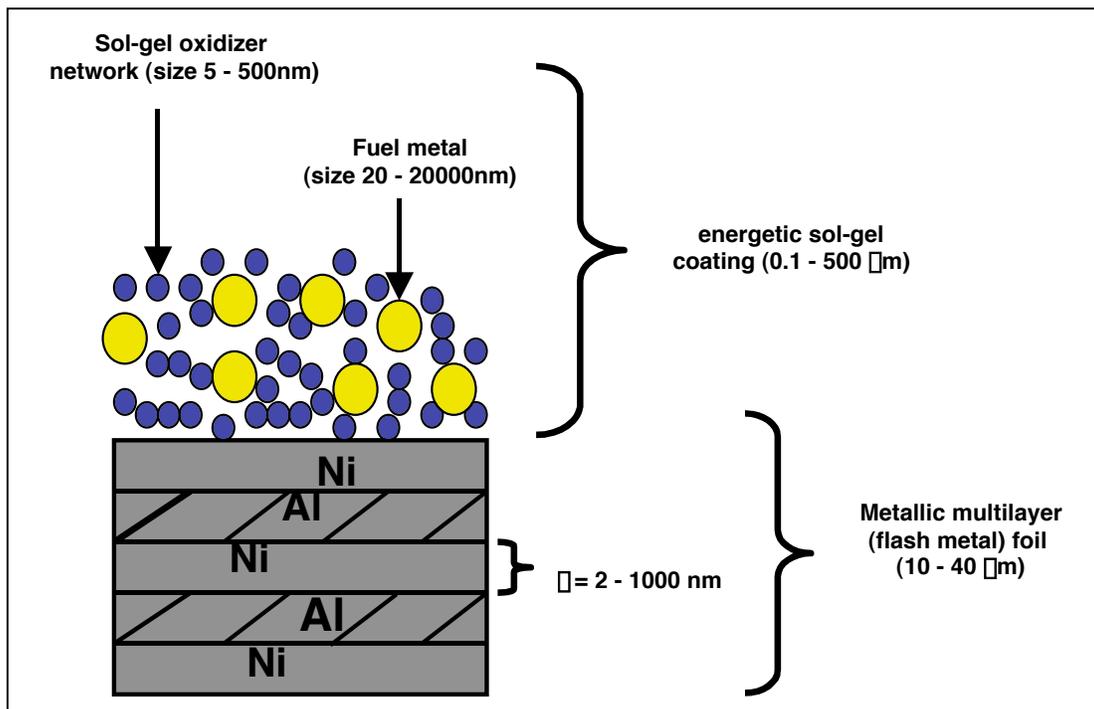


Figure 6. Scheme of microstructure of an energetic sol-gel coated flash metal multilayer nanocomposite for use as new, small, safe, and non-toxic initiators.

We have successfully used both ultra fine grained (UFG) nanometer-sized ($\sim 30\text{-}100\text{nm}$ diameter) Al and *conventional micron-sized Al* in these types of nanocomposites. It is important to emphasize that these materials can be made successfully using micron-sized Al. Micron-sized Al has been demonstrated to be an effective and reliable component of energetic materials. Although less reactive than the MIC Al, the micron Al has a greater energy density, is safer to work with, and has better aging properties all of which result in more reproducible performance in applications.

The photo in Figure 7a shows a Ni/Al multilayer structure foil that has been dip-coated with energetic sol gel material $\text{Fe}_2\text{O}_3/\text{Al}$.

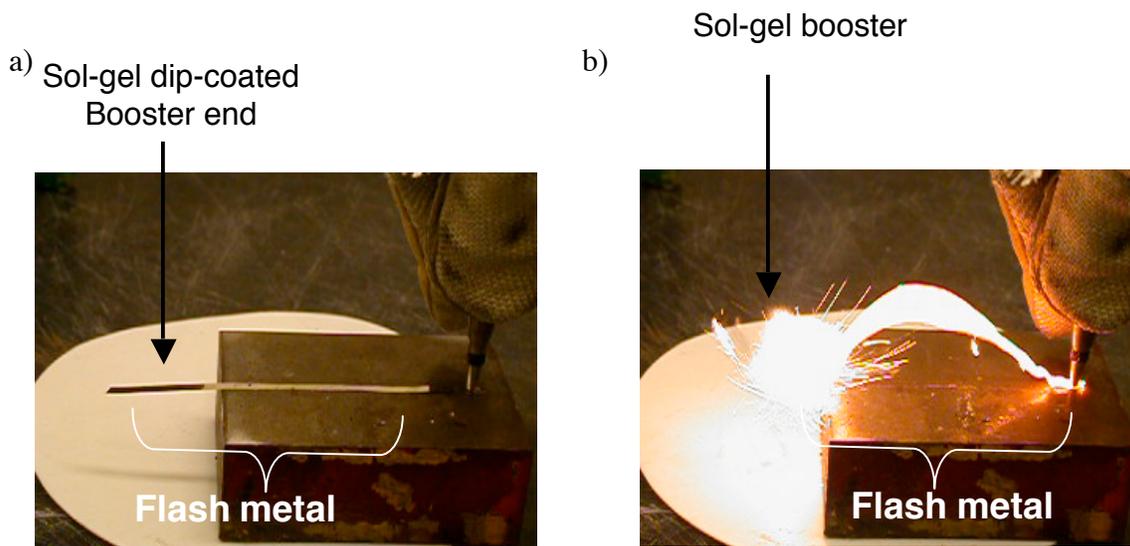


Figure 7. a) Sol-gel $\text{Fe}_2\text{O}_3/\text{Al}$ coated Ni/Al multilayer nanocomposite (the coated portion of the multilayer is on the left end of the foil and b) mechanical initiation of the nanocomposite, using a spring-loaded punch, results in ignition of the energetic sol-gel coating.

In Figure 7b we have used a spring-loaded punch to mechanically initiate the multilayer foil to react. As can be seen from the image, the mechanical stimulus induces the exothermic transformation of the multilayer to its respective intermetallic alloy. The arching glowing foil indicates that the transformation propagates along the foil perpendicular to the punch and migrates to the energetic sol-gel-coated region of the foil. This reaction has sufficient output energy to ignite the more energy dense sol-gel thermite reaction.[12] This particular thermite reaction is known to reach temperatures in excess of $3100\text{ }^\circ\text{C}$. Such composite material(s) should have sufficient energy output, hot particle ejection, and pressure pulse, when ignited, to initiate transfer charges, such as lead azide.

The initiation mixture components and their reaction products, from this particular nanocomposite, are non-toxic, non-hazardous and environmentally benign. The base $\text{Fe}_2\text{O}_3/\text{Al}$ composite and its reaction products Al_2O_3 and Fe metal are frequently used in many common industries on a commodity scale. The precursor compounds utilized in the preparation of the sol-gel materials are prepared from the inorganic metal salts (e.g., ferric chloride and ferric nitrate) are economical, non-toxic, safe, and easy to handle and dispose of.[10,11] The solvents used in the synthesis can be water or simple alcohols like ethanol. These solvents are advantageous as they are non-toxic, non-

hazardous, cost-effective, and do not pose any major disposal problems. The multilayer flash metal foil used in this case consists of alternating layers aluminum and nickel. The mechanical stimulus initiates the rearrangement of the multilayers to their alloy Al_3Ni_2 , which is an inert safe solid material. The components and their reaction products do not have the handling, disposal, and toxicity problems of NOL-130 components.

Publications

Portions of the work accomplished in FY03 were presented in a technical paper and published proceedings from the 34th Annual meeting of the Franunhofer Institut fur Chemiche Technologie in Karlsruhe, FGR in the summer of 2003.[13]

Summary

We are encouraged with the progress of the project to date. One promising candidate material has been identified, shown to have reasonable firing energy, and characterized via thermal and physical methods. Attempts to optimize this system to ensure successful initiation of a transfer charge are in progress. Those include detailed thermal and structural analyses to attempt to understand the relationship between structure and sensitivity and energy output. In addition, this material has been coated with a more energy dense sol-gel film to examine that effect on performance. Reliable and safe methods were developed to process sheets of energetic nanolaminate into test pieces with desired sizes and geometries. A drop ball apparatus was constructed at LLNL for the rapid evaluation of materials to identify promising candidate materials to be transitioned to the Army. We have successfully demonstrated the coupling of the two nanotechnologies to produce a device that in qualitative tests appears to function reliably. In addition, we have discovered that the energetic output of the nanolaminate reaction is sufficient to ignite the more energy dense and hotter sol-gel thermite reaction. Finally, we continue to have a strong collaboration with ARDEC that includes frequent discussions and updates via phone and email.

References

1. Cooper, P.W. *Explosives Engineering*, Wiley-VCH, New York. **1996**, p.323-326.
2. Mann, A.B.; Gavens, M.E.; Reiss, M.E.; Van Heerden, D.; Bao, G.; Weihs, T.P. *J. Appl. Phys.* **1997**, 82(3), 1178.
3. Gavens, A.J.; Van Heerden, D.; Mann, A. B. ; Reiss, M.E.; Weihs, T.P. *J. Appl. Phys.*, **2000**, 87(3), 1255.
4. Barbee, T.W., Jr.; Weihs, T.P. **1996**, U.S. Patent 5,547,715.
5. Barbee, T.W., Jr.; Weihs, T.P. **1996**, U.S. Patent 5,538,795.

6. Simpson, R.L.; Tillotson, T.M.; Satcher, J.H., Jr.; Hrubesh, L.W.; Gash, A.E. *Int. Annu. Conf. ICT (31st Energetic Materials)*, Karlsruhe, Germany, June 27-30, **2000**.
7. Gash, A.E.; Simpson, R. L.; Tillotson, T.M.; Satcher, J.H., Jr.; Hrubesh, L.W. *Proc. 27th Int. Pyrotech. Semin.* Grand Junction, CO, July 15-21, **2000** p.41-53.
8. Tillotson, T.M.; Gash A.E.; Simpson, R.L.; Hrubesh, L.W.; Thomas, I.M.; Poco, J.F. *J. Non-Cryst. Solids* **2001**, 285, 338-345.
9. Tillotson, T.M.; Hrubesh, L.W.; Simpson, R.L.; Gash. A.E., Patent application #S.N. 09/586,426
10. Gash, A.E.; Tillotson, T.M.; Satcher, J. H., Jr.; Hrubesh, L. W.; Simpson, R. L. *Chem. Mater.* **2001**, 13, 999.
11. Gash, A.E.; Tillotson, T.M.; Poco, J. F.; Satcher, J. H., Jr.; Hrubesh, L. W.; Simpson, R. L. *J. Non-Cryst. Solids* **2001**, 285, 22-28.
12. Fisher, S.H.; Grubelich, M.C. *Proc. 24th Inter. Pyrotech. Sem.* **1998**, 231.
13. Barbee, T.W. Gash, A.E.; Satcher, J.H.; Simpson, R.L. *Proceedings from the 34th ICT Meeting*, Karlsruhe, FGR, June 24-28. 31-1.