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# Stab Sensitivity of Energetic Nanolaminates

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## Abstract

This work details the stab ignition, small-scale safety, and energy release characteristics of bimetallic Al/Ni(V) and Al/Monel energetic nanolaminate freestanding thin films. The influence of the engineered nanostructural features of the energetic multilayers is correlated with both stab initiation and small-scale energetic materials testing results. Structural parameters of the energetic thin films found to be important include the bi-layer period, total thickness of the film, and presence or absence of aluminum coating layers. In general the most sensitive nanolaminates were those that were relatively thick, possessed fine bi-layer periods, and were not coated. Energetic nanolaminates were tested for their stab sensitivity as freestanding continuous parts and as coarse powders. The stab sensitivity of mock M55 detonators loaded with energetic nanolaminate was found to depend strongly upon both the particle size of the material and the configuration of nanolaminate material, in the detonator cup. In these instances stab ignition was observed with input energies as low as 5 mJ for a coarse powder with an average particle dimension of 400  $\mu\text{m}$ . Selected experiments indicate that the reacting nanolaminate can be used to ignite other energetic materials such as sol-gel nanostructured thermite, and conventional thermite that was either coated onto the multilayer substrate or pressed on it. These results demonstrate that energetic nanolaminates can be tuned to have precise and controlled ignition thresholds and can initiate other energetic materials and therefore are viable candidates as lead-free impact initiated igniters or detonators.

## Introduction

Energetic nanolaminates are nanocomposites that consist of hundreds of alternating nanoscale layers of metals.[1,2] Typically the alternating layers are made up of pairs of elements that undergo strongly exothermic reactions to produce the respective intermetallic product, one common example being the nickel/aluminum bimetallic structure. These structures can be fabricated by several physical vapor deposition techniques, with the most common one applied being magnetron sputtering.[3] These structures are ignitable via a number of

suitable stimuli and once reacted generate enough local heating to self-propagate through the entire structure.[4]

The drawing shown in Scheme 1 details the important structural features of an energetic multilayer. The distance  $T$  gives the total thickness of the foil sample. The distance corresponding to bi-layer thicknesses is referred to as the period,  $\Lambda$ , 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. Another feature of energetic multilayer thin films is the pre-reaction zone,  $\delta$ . This region exists at the interface of adjacent layers of the multilayer and is made up of a thin layer of the reacted intermetallic product formed during vapor deposition. The



**Scheme 1.** The structural features of an energetic multilayer: The distance  $T$  is the total thickness of the multilayer,  $\Lambda$  is the period or the repeating structural unit of the multilayer, and  $\delta$  is the pre-reaction zone.

thickness of this region, relative to the overall period, is very important to the overall energy and burn front propagation velocity of the energetic nanolaminate.[1,2,5,6] Finally, some nanolaminate materials can be top and or bottom coated with several additional layers of a single metal (in our case it was Al).

Selected combinations of metals in energetic nanolaminates can be prepared with energy densities as high as  $21.7 \text{ kJ/cm}^3$ , very high adiabatic reaction temperatures ( $\sim 3000 \text{ K}$ ), have high mechanical strength, and excellent aging characteristics.[7,8] Their sensitivity towards ignition, total energy, and reaction temperature can be readily and widely tuned, which make them attractive for many applications involving energetic materials. One such application is tunable ignition sources for explosive, propellant, or pyrotechnic charges. This application of energetic nanolaminates has been proposed previously in a number of patents over the past decade. [2,10,11] However, to our knowledge no study has been performed to more closely examine their application to one of these potential uses.

The application of energetic nanolaminates to mechanically activated energetic systems has an additional benefit in that it addresses an expressed desire to remove highly toxic materials from the military arsenal.[12] The common stab mix used in M55 stab detonators is NOL-130. This is made up of lead styphnate (basic) 40%, lead azide (dextrinated) 20%, barium nitrate 20%, antimony sulfide 15%, and tetrazene 5%.[13] 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.

The work reported may help address this by quantifying the stab ignition behavior of energetic nanolaminates and the important parameters that define it for one class of impact initiated device: the stab detonator. This study examines the effects of nanolaminate structure, composition, and physical form on their sensitivity towards stab initiation and standard small-scale safety tests for energetic materials. The results demonstrate that the stab sensitivity of energetic nanolaminates can be tailored over a wide range of impact energies. In addition, the energy output from these reacting materials can be used to initiate other energetic materials.

## Experimental

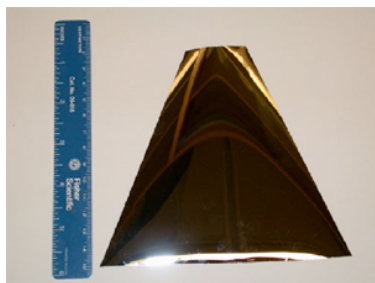
Energetic nanolaminate thin films were fabricated using the physical vapor deposition technique of magnetron sputtering. More specific details of this method are published elsewhere. [1-3] Two different energetic multilayer compositions were studied here. One was a bimetallic structure consisting of alternating layers of aluminum metal and a nickel-vanadium alloy (93 wt.% Ni, 7 wt.% V). The other composition consisted of aluminum and Monel 400 alloy (66.5 wt.% Ni, 31 wt. %Cu, 2.5 wt % Fe, trace amounts of C, Mn, Si, and S).

The energetic nanolaminates in this study were recovered after deposition as

freestanding metallic foils, like the piece shown in Figure 1a.

In this form they provide a number of processing options. Single 3 mm diameter disks of energetic multilayer were punched out of the foil. In addition a shear press was used to divide the foil into a coarse powder and sieves were used to isolate certain size particle size fractions of the powdered multilayer material, like that shown in Figure 1b.

a)



b)



**Figure 1.** Photos of a) free-standing energetic multilayer foil (ruler is 15 cm long) and b) a coarse powder of energetic multilayer (particle widths  $\sim 400 \mu\text{M}$ ).

Screening of the stab sensitivity of energetic nanolaminates was done using a definitive procedure. Energetic nanolaminate, in two different geometries (e.g., disks or powder form), were assembled in a given configuration in the bottom of a standard M55 detonator cup to make mock detonators. The total mass of energetic nanolaminate utilized in all configurations was between 12 to 20 mg. The configuration was then tamped down in the cup, before the surrogate powder was

pressed on top of it. On top of the multilayer initiating portion of the device a surrogate powder was pressed (in the case of live detonators this is where the transfer charge would be pressed). Talc was used as the surrogate powder. After loading of the surrogate material the powder was pressed at  $\sim 500$  psi and then an aluminum lid was crimped on to seal the device. To ensure that pressing of the energetic nanolaminate did not lead to ignition a selected mock detonators were opened instead of firing for visual examination to ensure no reaction on pressing. In all cases tested, the ignition of the energetic nanolaminate upon pressing was not observed. All mock detonator tests reported here were loaded using this procedure.

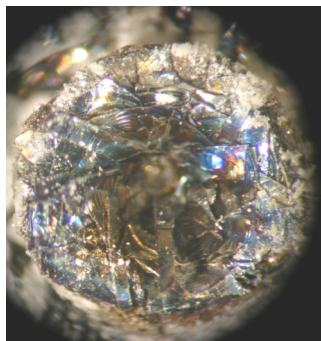
Each mock stab detonator was evaluated using a drop-weight test. In this test, a stainless steel ball weighing one ounce (28.35 g) is dropped from an adjustable height onto the standard steel firing pin ( $\sim 90 \mu\text{m}$ ) used in M55 detonators, which is held in place using a disposable plastic holder. The holder orients the pin directly above the detonator cup where the head is in position to be struck flush by the falling ball and the tip in contact with the bottom of the cup poised to pierce and drive into the device. Once the mock detonators have been fired a visual inspection of the energetic nanolaminate stab mix is required to determine if initiation was successful or not.

Since the tests were done on mock detonators “go” and “no-go” results were determined by visual inspection of the initiating mix after firing. This evaluation is quite straightforward as the visual appearance of the materials after reaction is drastically different than before. Figures 2a and 2b illustrate this point

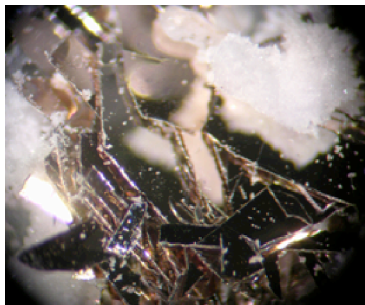
Powders from the stabbed reacted foils tend to fuse together into one large plug that has been significantly deformed and is shown in Figure 2a. In addition, the reacted materials display distinctive coloring possibly due to birefringence and often display ripples due to thermal wave propagation. Alternatively unreacted multilayer material is brittle, planar, and has no trace of discoloration as is shown in Figure 2b.

In some cases, reactive energetic multilayer parts were coated with thermitic composition ( $\text{Fe}_2\text{O}_3$  (35 wt%), Al (28 wt %), Ni (31 wt %) and Zonyl<sup>TM</sup> fluoropolymer (6 wt%) from DuPont Chemical Co.) using a solution containing an organic binder.

a)



b)



**Figure 2.** Photos of a) stabbed and reacted nanolaminate and b) stabbed and unreacted nanolaminate.

The response of energetic nanolaminates to friction was evaluated using a BAM high friction sensitivity tester. [14] The tester utilizes a fixed porcelain pin and a movable porcelain plate that performs a reciprocating motion. Weights are attached to a torsion arm allows for the applied force to be varied from 0.5 to 36 kg. The measure of frictional sensitivity of a material is based upon the largest pin load at which less than two ignitions occur in ten trials. The friction tester results are compared to an RDX calibration sample, which was found to be zero events in ten trials at 16.0 kg.

The sensitivity of energetic nanolaminates toward electrostatic discharge was measured on a modified Electrical Instrument Services electrostatic discharge

tester. A single square (0.4 cm x 0.4) of nanolaminate was loaded into Teflon washers and covered with 1 mm thick Mylar tape. A spark discharge of variable energy is sent from a movable electrode tip to the sample. The sensitivity is defined as the highest energy setting at which ten consecutive “no-go” results are obtained. The lowest energy setting for this instrument is 0.04 J the highest 2 J.[15]

The impact sensitivity of energetic nanolaminate foil squares were evaluated with an Explosives Research Laboratory Type 12 Drop Weight apparatus. The instrument is equipped with a Type 12A tool and a 2.5 kg weight. Squares of foil were placed on a piece of carborundum paper on a steel anvil and the weight dropped on them. The operator made visual evaluations for “go” and “no-go” events. The mean height for “go” events called the “50% Impact Height” denoted  $\text{DH}_{50}$  was determined using the Bruceton up-down method.[16] Results were compared to calibrated samples of PETN, RDX, and Comp-B whose  $\text{DH}_{50}$  values are 15.5 cm, 34.5 cm, and 41.4 cm respectively.

## Results and Discussion

### *Small-scale safety testing*

Small scale testing of energetic materials is done to determine their sensitivity to various stimuli including friction, spark, impact, and an elevated thermal environment. These tests are of extreme importance for several reasons, but mainly to establish important parameters for safe handling, processing, and storage. Table 1 contains a summary of the small-scale safety test results and structural parameters for the selected energetic multilayers examined in this study. There are several important conclusions that can be drawn from the data in Table 1.

In general, regardless of structure, all of the energetic nanolaminates have very a similar decomposition onset temperature of ~ 200 °C. Another common trend, amongst all nanolaminates considered, is the very high sensitivity to spark stimulus they all

displayed. As can be seen, regardless of structural parameters spark stimulus is a hazard that must be considered when dealing lower spark sensitivity limit was not realized

**Table 1.** Summary of energetic nanolaminate specimens their structural parameters and small-scale safety characteristics.

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

from these tests as our spark apparatus does not measure below 0.04 J.

It is not surprising that the energetic multilayers are spark sensitive as there are numerous studies that use spark stimulus as a method of ignition.[1,2,4] While this is an important hazard to consider it is one that has been dealt with effectively with current impact initiated device component materials. For example, both lead azide and lead styphnate, two of the stab mix ingredients that the energetic nanolaminates propose to replace are extremely spark sensitive with spark sensitivity levels of 0.0002 J and 0.0009 J, respectively.[17] From the data presented in Table 1 it does not appear that the structure of the multilayer has any effect on its spark sensitivity.

Alternatively, both the impact and friction sensitivities of the energetic nanolaminates are dependent on their respective nanostructures. As a whole, the nanolaminates with thinner layers of

reactant materials and no overcoats are much more sensitive to impact and friction than those with thicker layers and capping layers of aluminum.

#### *Stab sensitivity of energetic multilayers*

Many energetic systems can be activated via mechanical means.[13,18] Percussion primers in small caliber ammunition and stab detonators used in medium caliber ammunition are just two examples. Typically a small amount of impact sensitive material is used in a device to initiate more powerful (but less sensitive) secondary energetic materials..

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 conical firing pin through the closure disc of the device and into the stab initiating mix. 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.

Energetic multilayers can be ignited by thermal, mechanical, and electrical stimuli. Although quite detailed analysis has been performed for the ignition of energetic multilayers initiated by localized thermal heating using a spark, laser pulse, or joule heating from electrical current, comparatively little has been reported on the parameters involved in the mechanical initiation of energetic multilayers [4,19-21] This is somewhat surprising as mechanical initiation has been demonstrated to be remarkably reliable in energetic systems for hundreds of years.[13] Mechanical ignition has some benefits over other means. It can be very reliable, low cost, and requires relatively simple components. A short review of the relevant literature on mechanical ignition of energetic multilayers is presented below.

Wickersham *et al.* first showed that the heterometallic films are initiated by mechanical impact of a tungsten carbide stylus on a zirconium/silicon bi-layer material.[20] This work revealed a strong correlation between ease of ignition and both bi-layer period and total multilayer thickness. In this report thicker multilayers with finer bi-layer periods were more easily ignited. Clevenger *et al.* report the impact initiation of nickel/amorphous silicon thin films, which are exothermically transformed to the crystalline Ni<sub>2</sub>Si, and correlate higher reaction front velocities with a combination of finer bi-layer periods and thicker foils.[21] Self-sustained reaction was only observed in free-standing films (e.g., no substrate) with bi-layer thicknesses less than 12.5 nm. In addition, the temperature at which Ni<sub>2</sub>Si exothermically crystallizes was a strong function of the layer thicknesses. van Heerden *et al.* report results for the mechanical ignition of Ni/Al multilayers induced by the impact of a tungsten carbide sphere on samples positioned on a hard

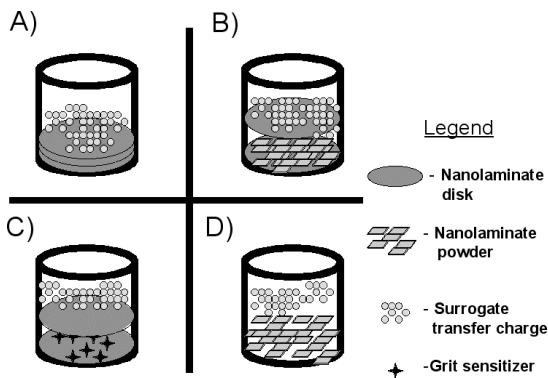
substrate.[4,22] The critical mechanical energy needed for ignition increased with bi-layer period with a minimum impact energy of ~4 mJ. It is clear from the previous work that the underlying nanostructure of the multilayer dictate its energy release and ignition properties. However there has been no detailed study as to the relationship between material parameters and the effects of stab impact initiation.

There is not a great deal known about the mechanism(s) of stab initiation of energetic materials. The most definitive study, by Chaudhri, strongly suggests that the mechanism of stab initiation is largely frictional.[23] In that system it was shown that frictional heating between adjacent energetic materials particles and not that between the steel striker tip and the energetic material particles is responsible for initiation. It was speculated that the large difference in thermal conductivity between the striker pin (metal: high thermal conductivity) and the NOL-130 mix (ionic salts and organic molecules: low thermal conductivity) leads to relatively low temperature generated at the pin particle interface relative to that generated between adjacent energetic particles subject to this force. Using that assumption, the challenge to get energetic metallic multilayers to initiate when being stab initiated by a steel pin may be difficult as both the pin and energetic material have high thermal conductivities, and therefore would be able to dissipate heat quickly and effectively, and thus would be less likely to generate local spots of high temperature to initiate a self-propagating reaction. Therefore the ability to tune the ignition threshold of these materials by structural modification is critical for this application.

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

Previous results from related work has established a suitable candidate energetic multilayer material for this application.[24] Of those energetic multilayers examined, the one with highly desirable properties for this application has a relatively thick structure (55  $\mu\text{m}$ ), possessed a fine bi-layer period ( $\sim 20$  nm), was uncoated, and has an Al/Monel composition.

Coarse powders of energetic multilayers with average sizes from 400-1500  $\mu\text{m}$  and disks 3 mm in diameter were used in mock detonator testing. With these two forms there were a number of configuration options available for stab detonator testing. Scheme 2 below summarizes the different energetic nanolaminate configurations examined.



**Scheme 2.** Configurations utilized in stab detonator testing: a) Disk, b) disk/powder/disk, c) disk/abrasive/disk, and d) powder configurations.

Results from the stab testing of mock M55 detonators demonstrate the importance of configuration on the minimum stab ignition energy. These results are summarized in Table 2.

Minimum stab energies for the nanolaminates ranged from 5 mJ to 74 mJ for the different configurations with the highest being for the disks alone and the lowest for powder alone. The addition of a high melting point grit

sensitizer (100  $\mu\text{m}$   $\text{Al}_2\text{O}_3$ ) served to lower the minimum stab energy for a configuration with only disks in it. This is a common practice and has been observed previously.[25] The small foreign particles have the effect of

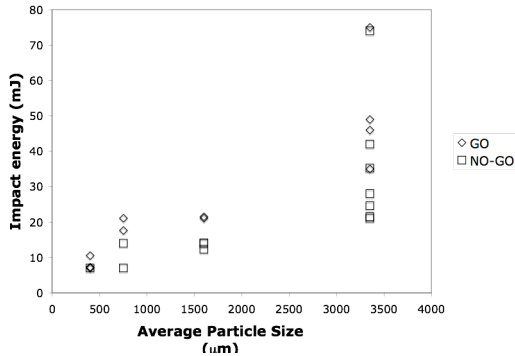
**Table 2.** Influence of stab configuration on minimum stab energy for a 55  $\mu\text{m}$ -thick Al/Monel energetic multilayer system with particle size of 400  $\mu\text{m}$ .

<b>Configuration</b>	<b>Minimum Stab Energy (mJ)</b>
A- Disks only	74
B- Disk/powder/disk	18
C- Disks w/ $\text{Al}_2\text{O}_3$ grit	32
D- Powder only	5

artificially introducing transient hot spots into the energetic material to sensitize it.

The data in Table 2 indicate that the incorporation of a coarse powder of energetic multilayer into the mock detonator drastically reduces the minimum firing energy of the mock device. There are several possible reasons for this. In all cases the firing pin must pierce the Al M55 cup, which dissipates some of the kinetic energy of the pin. However, in the case of configuration D (powder only) the remaining energy of the firing pin is transferred into the powder. In all of the other configurations the pin must pierce another barrier(s), namely the center of the disks of nanolaminate, and thus loses additional kinetic energy. Even though that energy goes into the energetic multilayer material the location of that energy transfer on the surface of the foil appears to be important. In fact, it has been previously reported that energetic nanolaminates were more easily and reproducibly initiated by impacts on the edge of the foil rather than in the body of the foil.[22]

The average particle size of the powdered energetic nanolaminate is a critical factor in their stab sensitivities. Figure 4 is a plot of average powder particle size versus impact energy for Al/Monel energetic multilayer material in configuration B (disk/powder/disk).



**Figure 4.** Plot of impact energy versus average particle size for an uncoated Al/Monel 400 multilayer material with a 20 nm bi-layer period, an overall thickness of 55 µm, and tested in configuration B.

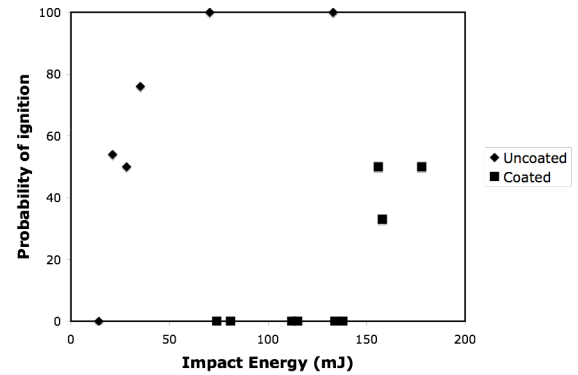
Although there is some scatter in the data the overall trend line indicates that impact energy needed for ignition decreases with decreasing average particle size of the nanolaminate powder.

There are a number of possible reasons that the use of a powdered energetic multilayer as opposed to larger disks leads to enhanced stab sensitivity of energetic nanolaminates.

The compacted powder is less dense than a stack of macroscopic foils. Therefore it is more easily pierced through by the firing pin and thus gets the more of the full effect of the tip/particle and interparticle frictional forces than a stack of disks. With a powder the frictional forces are enhanced relative to stacked monoliths. Friction between surfaces is due to a combination of adhesion and plastic deformation. Adhesion can only occur at regions of contact and plastic deformation is caused by grooving, cracking, or ploughing of rough surfaces or

edges. In the powdered energetic nanolaminate these interactions should be enhanced as the particle size decreases which likely leads to the observed increase in stab sensitivity. Another possible reason for the increase in sensitivity is increased impactor tip/nanolaminate edge interactions with the powdered material. A particle edge is more easily deformed than the center of a monolith. By decreasing the particle size of the nanolaminate foil the number of edges that interact with the impactor pin are increased leading to more possible initiation sites.

The data in Table 2 and Figure 4 clearly indicate that the stab sensitivity of the energetic multilayers is tunable. Another important parameter in the evaluation of stab igniters and detonators is their probability of initiation at the given energy input levels. A series of impact ignition tests were conducted on energetic multilayer systems with an alternative composition, Al/Ni(V). Experiments were run at a variety of impact heights and the data was plotted as probability of ignition versus impact energy. Figure 5 contains this information for two sets of Al/Ni(V) energetic



**Figure 5.** Probability of ignition of Al/Ni(V) energetic multilayer in configuration B. Each data point is derived from 5 to 35 separate trials.

multilayers. Both materials have identical multilayer periods of 19 nm however the total thickness of the films are different 24

$\mu\text{m}$  as compared to  $9 \mu\text{m}$ . In addition, the  $9 \mu\text{m}$  material has been over-coated with  $800 \text{ nm}$  of Al whereas the  $24 \mu\text{m}$  material was not overcoated. This is reflected in the DSC data for each material that show the coated material has a total reaction energy about 20% lower than that of the uncoated (see Table 1).

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

The over-coating has the effect of desensitizing the energetic nanolaminate towards mechanical initiation. One can postulate at least two reasons for this observation. The overcoating of Al must act as an inert heat sink that adds no heat to the reaction wave that begins with heating from the localized mixing of the bi-layers induced by plastic deformation. The reaction only self propagates if heat is generated faster than it dissipates to the surroundings. Alternatively, the overcoat layers may act to buffer the intermixing of adjacent layers from frictional interactions as the deformation of the surface layers do not result in exothermic output.

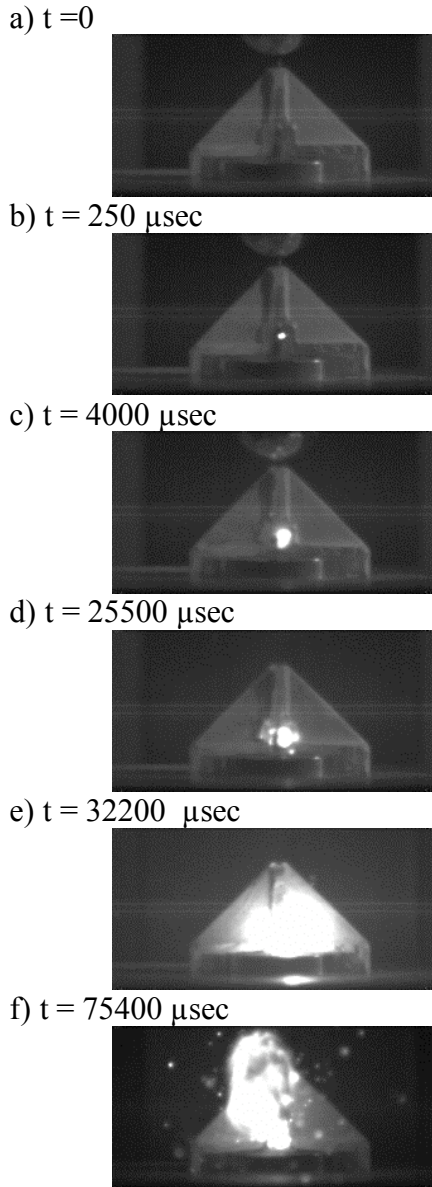
### ***Energetic coatings***

The work described here as well as elsewhere recognizes and demonstrates the ability to tailor the ignition threshold of energetic multilayers.[24] Therefore these materials hold promise for use in stab detonators, primers, and igniters. However in all of these applications the energetic multilayer must be capable of igniting of initiating the next energetic material in the energy output train. The reacting multilayer undergoes solid-state combustion (gasless) and therefore energy transfer must be

accomplished by thermal conduction or radiation. In many cases it would be desirable to transfer energy through the ejection of hot particles and gases. This desired effect can be accomplished by coating the energetic multilayer materials with thermite that is deposited by sol-gel processing or painting techniques. Here the energetic multilayer serves as the precision igniter and the energetic sol-gel functions as a low-cost, non-toxic, non-hazardous booster in the ignition train.

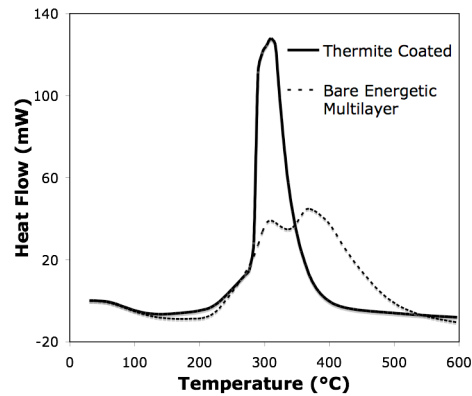
The thermal initiation and explosion temperatures and time to reaction is known for a number of transfer charge explosives, propellants, and pyrotechnics.[18] Therefore it would be useful to know the thermal evolution and time frame for that reaction in nanolaminate coated with thermite and initiated by stab. With that in mind experiments were done to determine the times to initiation, for maximum output, and total duration of the reaction, respectively.

Figure 6 contains a series of still frames from a high speed video of the stab ignition of energetic multilayers that have had a powdered mixture of aluminum, iron (III) oxide, nickel, and Zonyl<sup>TM</sup> (fluoropolymer) pressed on top of it. The series of still images in Figure 6 capture the two-stage reaction of coated energetic nanolaminates. The first visible sign of ignition was observed at  $250 \mu\text{sec}$  in Figure 6 b. Once ignited the packed energetic multilayer powder self-propagates as is shown by the growing luminous plume in Figure 6c. The first visible sign of thermite ignition follows in Figure 6d at  $25500 \mu\text{sec}$ . The secondary thermite reaction is observed to continue out to at least the  $75000 \mu\text{sec}$  time frame. Visible hot particle ejection and a gas plume generated from the decomposition of the fluoropolymer characterize the energy release captured in Figure 6f.



**Figure 6.** Still frames from a high-speed video of the ball-drop impact ignition of energetic nanolaminate pressed powder that is in contact with a fluoropolymer-containing thermite.

Further investigation of the energy release properties of the thermite coated energetic multilayer material was performed using differential scanning calorimetry (DSC). Figure 7 is an overlay of DSC traces of samples of Al/Ni(V), and Al/Ni(V) energetic nanolaminate coated with thermite heated at a rate of  $200^\circ\text{C}/\text{min}$ .



**Figure 7.** Differential scanning calorimetry traces for bare Al/Ni(V) multilayer and that coated with a thermite.

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

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

## Conclusions

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

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