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**TITLE AND SUBTITLE**  
Final Report: Multiphase Combustion of Metalized Nanocomposite Energetic Materials

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**ABSTRACT**  
This project examines multiphase ignition and combustion of aluminum fuel particles and focuses on (1) characterization of energy transport and Al oxidation in a variety of initiation scenarios; (2) diagnostic development to quantify thermal and electrical properties of reactants and reactions; (3) theoretical development of mechanisms promoting Al reactivity; and, (4) design and synthesis of Al particles and composite mixtures (and thin films) tailored toward improved reactivity according to theoretical strategies. Results focus on energetic thin film synthesis, electrostatic discharge ignition sensitivity coupled with new measurements of electrical conduction. New

**SUBJECT TERMS**  
Aluminum Particles, Energetic Composites, Combustion, Ignition, Equilibrium Analysis, Flame Speeds, Reactivity, Fluoropolymers, Metal Oxides

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- REPORT UU
- ABSTRACT UU
- THIS PAGE UU

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**NUMBER OF PAGES**  
19a. NAME OF RESPONSIBLE PERSON  
Michelle Pantoya

**TELEPHONE NUMBER**  
806-742-3563

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Final Report: Multiphase Combustion of Metalized Nanocomposite Energetic Materials

ABSTRACT

This project examines multiphase ignition and combustion of aluminum fuel particles and focuses on (1) characterization of energy transport and Al oxidation in a variety of initiation scenarios; (2) diagnostic development to quantify thermal and electrical properties of reactants and reactions; (3) theoretical development of mechanisms promoting Al reactivity; and, (4) design and synthesis of Al particles and composite mixtures (and thin films) tailored toward improved reactivity according to theoretical strategies. Results focus on energetic thin film synthesis, electrostatic discharge ignition sensitivity coupled with new measurements of electrical properties, new diagnostics for 2D thermal mapping of reactions, new results for resolving exothermic surface chemistry between the alumina passivation shell surrounding Al particles and halogenated oxide species, and new results targeting further development of mechanisms promoting Al reactivity.
Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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<tr>
<td>08/21/2013 27.00</td>
<td>Eric Collins, Michelle L Pantoya, Andreas Neuber, Michael Daniels, Daniel Prentice. Piezoelectric Ignition of Nanocomposite Energetic Materials, Journal of Propulsion and Power,   (08 2013): 0. doi:</td>
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<td>12/19/2014 39.00</td>
<td>Nicholas Clayton, Keerti Kappagantula, Michelle Pantoya, Sharon Kettwich, Scott Iacono. Preparation, Characterization, and Energetic Properties of Metallized Nanofibers, ACS Applied Materials and Interfaces,   (01 2014): 6049. doi:</td>
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12/19/2014 38.00 Charles Crane, Keerti Kappagantula, Michelle Pantoya. Determination of Spatial Distribution of Temperature from Combustion Reactions: A Diagnostic Study, Review of Scientific Instruments, (10 2013): 84705. doi:


TOTAL: 21

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:
(c) Presentations

All presentations were published and are reported. Students gave approximately 25 presentations on this work during this award period.

**Number of Presentations:** 0.00

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<td>08/20/2012 7.00</td>
<td>Cory Farley, Michelle Pantoya. Reaction Kinetics of Nano-energetics with Halogen Containing Oxides, Central States Section of the Combustion Institute. 22-APR-12, .</td>
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<td>08/20/2012 10.00</td>
<td>Jeffrey Gesner, Michelle Pantoya. THE INFLUENCE OF OXIDE SHELL THICKNESS ON NANO-ALUMINUM COMBUSTION BEHAVIOR, JANNAF 59th JPM/41st SMBS / 37 PEDCS / 28th RNTS / 26th SEPS Joint Subcommittee Meeting. 04-MAY-12, .</td>
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Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

08/20/2012 1.00 Charles Crane, Eric Collins, Michelle Pantoya, Brandon Weeks. Nanoscale Investigation of surfaces exposed to a thermite spray, Applied Thermal Engineering (06 2011)


08/20/2012 4.00 Birce Dikici, Michelle Pantoya, Benjamin Shaw. Analysis of the influence of nanometricaluminium particle vaporisation onflame propagation in bulk powdermedia, Combustion Theory and Modelling (10 2011)

08/20/2012 5.00 Keerti Kappagantula, Michelle Pantoya. Experimentally measured thermal transport properties ofaluminum–polytetrafluoroethylene nanocomposites with grapheneand carbon nanotube additives, International Journal of Heat and Mass Transfer (11 2011)


08/21/2013 17.00 Chelsea Weir, Michelle L. Pantoya, Michael A. Daniels. The Role of Aluminum Particle Size in Electrostatic Ignition Sensitivity of Composite Energetic Materials, Combustion and Flame (05 2013)

08/24/2013 30.00 Kelsey Meeks, Michelle L Pantoya, Christopher Apblett. Deposition and Characterization of Energetic Thin Films, Journal of Power Sources (07 2013)


08/27/2012 12.00 Michelle Pantoya, Valery Levitas, Jeffrey Gesner. Effect of oxide shell growth on nano-aluminum thermite propagation rates, Combustion and Flame (04 2012)


TOTAL: 14

Number of Manuscripts:

Books

Received Book


TOTAL: 1

Received Book Chapter


TOTAL: 1

Received Book


08/21/2013 29.00 Oliver Mulamba, Michelle L. Pantoya. Combustion Characterization of Energetic Fluoropolymer Composites, United States of America: John Wiley & Sons, Inc., (06 2013)

TOTAL: 2

Patents Submitted

Patents Awarded
Awards
M.L. Pantoya: J. W. Wright Regents Endowed Chair; Discovery Channel Daily Planet segment "Green Ammunition"; Outstanding Researcher Award, Texas Tech University 2011-2014; featured on PBS Kids as Dr. Michelle the Engineer.

## Graduate Students

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<td>Jesus Cano</td>
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Student Metrics
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The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 3.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 4.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: ...... 0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense...... 2.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ...... 2.00

Names of Personnel receiving masters degrees

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Names of personnel receiving PHDs

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Names of other research staff

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Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment
Technology Transfer

See Attachment
Multiphase Combustion of Metalized Nanocomposite Energetic Materials

Michelle L. Pantoya
Mechanical Engineering Department
Texas Tech University, Lubbock, TX 79409

Forward

The students of the Energetic Materials Combustion Laboratory at Texas Tech University and myself, Dr. Michelle Pantoya are deeply grateful for the opportunity to work on Army relevant research that has significantly contributed to the advancement of energetic materials science. Graduates supported in this project have gone on to work for Army labs (Aberdeen Proving Ground – Dr. Eric Collins); the national laboratories (Sandia – Dr. Shawn Stacy, LANL – Drs. Cory Farley and Charles Crane); academia (West Texas A&M University – Dr. Oliver Mulamba and Ohio University – Dr. Keerti Kappagantula); and industry. Many of our contributions are being patented and transitioned to field applications (via Idaho National Laboratory). Also, our publications from this work to date have been cited over 2000 times in the archival literature.

The scientific contributions marked by our many publications are rivaled by the quality of the future energetic material scientists that have been taught and trained in our laboratory and will benefit this country for future generations. I am also eternally grateful to encouragement and support from my program manager, Dr. Ralph Anthenien who critically and constructively always keeps us on our toes and challenges us to think from different perspectives. Also, my sincere gratitude toward Dr. David Mann, who helped me get my start in this field 10+ years ago.

The Energetic Materials Combustion Lab celebrated their 15th anniversary of its founding at Texas Tech this month. We are currently in the process of over $200,000 of laboratory renovations that will bring the lab into state of the art functionality and appearance. Our group is thankful to ARO and our collaborators that help make our progress possible. Thank you for your support.

Warmest wishes,
Michelle Pantoya
J. W. Wright Regents Endowed Chair
Professor & Director, TTU Combustion Lab

Vision:
Advancing energetic materials science
for the safety of people and the environment
Archival journal publications under this contract:


August 2014
From left to right: Jesus Canos, Cory Farley, Kade Poper, Michelle Pantoya, Keerti Kappagantula, Evan Vargas, Jena McCollum, Billy Clark, Michael Bello.


Scientific progress and accomplishments

Progress towards understanding combustion of nanocomposite energetic materials and their role in weapon systems has been made through understanding the processes controlling ignition, energy propagation, reaction kinetics specific to aluminum fuel particles and theoretical development of reaction mechanisms. In the following discussion a summary of the results learned for the 2011-2014 project duration will be highlighted as well as students leading the investigations and publications detailing each study. The results are summarized in Items (1) – (4).

(1) Energy Transport Studies
   a. Thermal properties of composites
   b. Impact ignition
   c. Electrostatic discharge ignition
   d. Laser ablation and ignition

(2) Synthesis & Reaction Kinetics
   a. Fluorine and aluminum reactivity
   b. Synthesis and characterization of fluoropolymer - aluminum particles

(3) Diagnostic Developments
   a. Two dimensional temperature mapping
   b. Heat flux sensor

(4) Modeling and Theory Development
   a. Melt dispersion mechanism
   b. Modeling of particle and powder reactions
(1) Energy Transport Studies

Research that resolves energy transport through particulate media addressed three basic phenomena all relevant to ignition and energy propagation. (a) The first focused thermal energy transport through particulate media and thermal property relevance to diffusion controlled reactions. (b) The second focused on the interaction of electrostatic energy with a composite energetic powder towards improving the safe handling of powders. (c) The third focused on ignition and laser ablation of energetic powders and compacts using a Nd-YAG laser pulse for high heating rate ignition and/or ablation.

a. Thermal properties of composites

Thermal transport properties in reactive materials as a function of fuel particle size and oxidizer composition were studied. Results show nano-Al composites are more insulative than their micron scale counterparts, exhibiting three times lower thermal conductivity in some cases. Second, there is a paradoxical relationship for thermal diffusivities: nanocomposites of Al+Fe₂O₃ and Al+Teflon show higher thermal diffusivities than their micron scale counterparts; but, Al+TiO₂ show higher thermal diffusivity for micron-composites. This is explained through investigating the nature of void space distributions within a compressed powder pellet. Larger void spacing reduces the inter-particle connectivity and hinders the speed of energy propagation. In all samples, the composites with larger void spacing exhibited lower thermal diffusivities. (lead student: Amanda Gordon)

The next study focused on Al/Teflon composites that were impregnated with carbon additives: amorphous nano carbon spheres (nano C), graphene flakes and unaligned multiwalled nano carbon tubes (CNTs). In this study our goal was to quantify thermophysical properties such as thermal conductivity, specific heat capacity and thermal diffusivity using a laser flash analysis diagnostic. Many formulations with CNTs do not exhibit high levels of thermal properties, such that measuring the fundamental properties of composites with these additives is relevant. The additives were selected based on their completely different structures. The Al/Teflon had an equivalence ratio of 1.4 and the cylindrical pellet samples had a TMD ranging from 75 to 80%. Additives in the quantities of 1, 5 and 10 mass % were introduced into the Al/Teflon matrix. Results show that graphene had the greatest influence on the thermophysical properties. Thermal conductivity of the composites containing graphene increased by 98%. Graphene similarly enhanced the thermal diffusivity and specific heat of the Al/Teflon matrix. On the other hand, nano C and CNTs decreased the thermal conductivity and thermal diffusivity of the samples significantly and did not have a significant effect on the specific heat capacity of the nanocomposites.

The different trends displayed by the additives with essentially same chemical composition were attributed to their markedly different structures. Nano carbon spheres are
amorphous with random sp2 and sp3 bonding with the carbon properties. Graphene and CNTs consist of sheets of sp2 bonded carbon. While graphene is single sheets of carbon atoms, CNTs are tubes obtained by rolling sheets of carbon atoms. Presence of graphene sheet-like flakes with very high thermal conductivity enhances the effective thermal conductivity of the nanocomposites. Although similar results were expected due to the presence of the CNTs, measurements suggested contrary. At higher loading, CNTs tend to agglomerate in the composites if they are unaligned. This agglomeration decreases the thermal transport and conductivity of the matrix. Since nano C are amorphous spheres with lower thermal conductivity compared to the Al/Teflon, their presence tends to disrupt the heat transport network and hence decreases the thermal conductivity. Since thermal diffusivity is a linear function of thermal conductivity, given that there are no significant changes in the heat capacity, diffusivity mirrors the trend of thermal conductivity of the nanocomposites as the results suggest. (lead student: Keerti Kappagantula)

Exploiting these transport properties is especially important for diffusion controlled reactions. For example, slow burning reaction that are being examined for their use as energy storage and delivery materials. For this application, non-gas generating mixtures that produce enough energy to sustain reaction propagation are ideal. A potentially promising formulation for this application is comprised of Manganese (Mn) powder mixed with Manganese dioxide (MnO2) because thermoequilibrium calculations predict the Mn/MnO2 reaction is non-gas generating and highly exothermic. The objectives of this study were to examine the flame propagation behavior of various mass percentages of Mn and MnO2 and evaluate the influence of fuel particle size. Results showed that conduction is the dominant energy transfer mechanism for the reaction even in the loose powder configuration regardless of fuel particle size. Combustion wave speed was measured as a function of composition and Mn particle diameter. Nanometric Mn particles (referred to as nano Mn) produced higher flame speeds than micron Mn particles for all the mass percentages of Mn studied. This behavior was attributed to the Manganese (II, III) oxide (Mn3O4) passivating shell around Mn particles which created an oxygen rich environment for the reaction zone. This finding is in contrast to nano-Al particles in which energy transfer is dominated by conduction (i.e., highly consolidated nanocomposite). For nano Al, the alumina (Al2O3) passivation shell does not participate in the oxidation reaction and instead acts to retard energy propagation as a heat sink. As a result, reducing the particle size of Al produces lower flame speeds. The combustion wave speed was found to be a maximum of 12.01 mm/s for the nano Mn/MnO2 reaction at a Mn mass percentage of 29%. Flammability limits are also defined. (lead student: Keerti Kappagantula)

b. Impact ignition

Impact ignition using a drop weight apparatus was investigated for energetic material composites of Al and Teflon with additives varying from CNTs, nano C and graphene. The composites containing even small amounts of CNT demonstrated a heightened sensitivity to impact ignition, with ignition energies on the order of 0.29 J. CNTs have high Young’s Modulus and may promote hot spot formation spurred by friction and shear interaction between CNTs and surrounding particles (i.e., at interfaces and grain boundaries). In contrast, graphene does not affect ignition energy or sensitivity until larger quantities are added to the composite. Graphene has a significantly higher thermal conductivity than the other additives which may promote diffusion of local thermal energy, reducing the likelihood of hot spot development. These results provide insight into factors that promote sensitivity to impact ignition thereby leading to advances in the safe handling of energetic materials. Further work is required since formation of hot spots is random on the surface being impacted and thus cannot be quantified. (lead student: Keerti Kappagantula)


c. Electrostatic discharge ignition mechanisms

Initial activities included the development of two benchmark diagnostics. The first measures electrostatic discharge (ESD) ignition delay time and minimum ignition energy (MIE) of powders or compressed pellets from ESD stimuli (Fig. 1A). The second enables accurate electrical conductance ($k_e$) measurements for DC input (Fig. 1B).

![Figure 1 A. Photograph of ESD ignition tester and B. schematic of electrical conductivity measurements of powders.](image)

Our first significant contribution showed a correlation between electrical conductance ($k_e$) and ignition sensitivity established through coupled measurements using these diagnostics. Results revealed a $k_e$ threshold range that triggers ignition. Findings are illustrated in Fig. 2A: (1) reducing Al particle size leads to higher electrical conductance (lower resistance) and reduced ignition energy (and delay time); (2) oxidizers such as CuO are the most electrically sensitive with highest measured electrical conductivity. The key to ignitability resides in the shell-core structure of the alumina-aluminum particles. Smaller Al particles provide more contact points for accumulated electrical energy to be transferred to the fuel causing reduced ignition energy (Fig. 2A).
2A). Results reveal for Al nanoparticles the alumina shell does not dissipate (resist) electrical energy as much as it acts as a capacitive network promoting the flow of current through the particle and random media (Fig. 2B). This is a key reason that nano-Al composites are exceptionally sensitive to ESD stimuli over their micron scale counterparts.

To control the electrical conductivity of the mixture and affect ESD ignition sensitivity, carbon additives (such as graphene and carbon nano-tubes (CNT)) were investigated in small concentrations. It was found that once the additive reached the percolation threshold for the
mixture, the increased electrical conductivity values reached a plateau (spurred by the connectivity of the highly electrically conductive additive). Only small concentrations were required to achieve percolation (i.e., < 2% by mass) such that the presence of this additive does not adversely influence the combustion behavior of the mixture. As an example, Fig. 3 shows results revealing heightened levels of electric conductivity with 4% graphene. However, CNTs were found to be more effective for achieving percolation at lower thresholds and controlling ESD sensitivity via electrical conductivity. On-going work will reveal how micron scale carbon fiber may replace (or couple with) CNTs and perhaps find greater utilization in applications.

Figure 3. Electrical conductivity of Al + PTFE with added GNP.

Tailoring a composites $k_e$ for controlled ESD sensitivity was examined for an insensitive mixture of aluminum and polytetrafluoroethylene (Teflon - or PTFE). The hypothesis is that creating a highly conductive network within the reactant matrix will channel electric current through the matrix before buildup and ignition can occur. For this work, an insensitive composite (Al+PTFE) with varying CNT additives was shown to exhibit a narrow range of $k_e$ controlled by additive concentration that produced ESD ignition (Fig. 4). This mixture was selected so that we could control $k_e$ and identify upper and lower bounds that cause ESD ignition.

Figure 4. Ignition sensitivity to ESD.
Conversely, we examined a highly ESD ignition sensitive composite (Al+CuO) with CNT additives and showed that at percolation, the mixture became desensitized to ESD stimuli (Fig. 5). Only CNT additives were found effective based largely on the tube like structure that promotes connectivity within the matrix of particles and achieves percolation at low concentrations (i.e., < 1 wt %).

As a side investigation we examined the response of an energetic powder to ESD stimuli generated from a piezo electric crystal (PZT). Results show that a high PZT dielectric strength leads to faster ignition times because of the higher voltage delivered to the energetic. Ignition delay is under 0.4 ms, which is faster than observed with thermal or shock ignition. Electric ignition of composite energetic materials is a strong function of inter-particle connectivity and thus the role of bulk density on ESD ignition sensitivity was a focus of this study. Results show that the ignition delay times are dependent on the powder bulk density with an optimum bulk density of 50%. Packing fractions and electrical conductivity were analyzed and aid in explaining the resulting ignition behavior as a function of bulk density.

**Provisional Patent**  

d. Laser ablation and ignition of composites

Laser flash analyses of reactant formulations show that there is a limit to the rate of energy absorption through nano-particulate powders in comparison with compressed pellets. In loose powders, thermal pathways are reduced and the photon interfaces between particles influence thermal diffusivity more than the thermal properties of the materials. This means that for ignition, thermal diffusivity is almost constant for loose powders but varies significantly as the powder is compacted into a pellet. *(lead student: Shawn Stacy)*

Thermal conductivity and absorption coefficients were determined for a range of bulk densities for consolidated aluminum (Al) nanoparticle pellets by a laser flash analysis technique. Samples where heated on their front face using a Nd:YAG laser (1064 nm wavelength) and the temperature was measured on the rear face as a function of time. COMSOL Multiphysics® was used to model the experimental setup to determine the thermal conductivity and absorption coefficients. Thermal conductivity was found to increase with density from 0.2 to 1 W/(mK) for densities from 1.1 to 2.3 g/cm³ due to increase surface contact between particles. The absorption coefficient was found to range from 0.30 to 0.54 and increase with density for the range of bulk densities investigated. These results provide a fundamental understanding of properties influencing ignition mechanisms in aluminum containing materials.

Laser ignition using the Nd:YAG to produce heating rates from $9.5 \times 10^4$ to $1.7 \times 10^7$K/s was also studied. This is a unique heating rate regime for laser ignition studies because most studies employ either continuous wave CO₂ lasers to provide thermal ignition or pulsed Nd:YAG lasers...
to provide shock ignition. In this study aluminum (Al) and molybdenum trioxide (MoO₃) nanoparticle powders were pressed into consolidated pellets and ignited using a Nd:YAG laser (1064nm wavelength) with varied pulse energy. Results show reduced ignition delay times corresponding to laser powers at the ablation threshold for the sample. Heating rate and absorption coefficient were determined from an axisymmetric heat transfer model. The model estimates absorption coefficients from 0.1 to 0.15 for consolidated pellets of Al+MoO₃ at 1064 nm wavelength. Ablation occurred for the highest heating rates and resulted from fracturing caused by a rapid increase in thermal stress and slowed ignition of the pellet.


(2) Synthesis & Reaction Kinetics

a. Resolving Reaction Kinetics of Aluminum with Halogen Oxidizers

Coupling molecular scale reaction kinetics with macroscopic combustion behavior is critical to understanding the influences of intermediate chemistry on energy propagation, yet bridging this multi-scale gap is challenging. This study integrates ab initio quantum chemical calculations and condensed phase density functional theory to elucidate factors contributing to experimentally measured high flame speeds (i.e., > 900 m/s) associated with halogen based energetic composites, such as aluminum (Al) and iodine pentoxide (I₂O₅). Experiments show a direct correlation between apparent activation energy and flame speed suggesting that flame speed is directly influenced by chemical kinetics. Towards this end, the first principle simulations resolve key exothermic surface and intermediate chemistries contributing toward the kinetics that promote high flame speeds. Linking molecular level exothermicity to macroscopic experimental investigations provides insight into the unique role of the alumina oxide shell passivating aluminum particles. In the case of Al reacting with I₂O₅, the alumina shell promotes exothermic surface chemistries that reduce activation energy and increase flame speed. This finding is in contrast to Al reaction with metal oxides that show the alumina shell does not participate exothermically in the reaction. First principle simulations show intermediate I₂O₅ decomposition and surface chemistries between I-O species and Al-Al₂O₃ core-shell particles are almost all exothermic. Also, Al can act as an effective intermediate to aid decomposition of iodine oxide species and aid in the production of I and I₂ in the gas phase. Results from this modeling study are consistent with the activation energy measurements which correlate inversely with flame speed.
This study examined the effect of atmospheric oxygen concentration on composite energetic material reactions that are controlled by the melt dispersion mechanism or the diffusion oxidation mechanism. High speed reactions which activate the melt dispersion mechanism show a smaller percent increase in flame speeds when exposed to a high oxygen atmosphere. Slower, diffusion limited reactions showed greater increases in flame speed by as much as 200% increase in a high oxygen atmosphere. A theoretical model for MDM was developed to predict the temperature corresponding to fracture of the alumina shell in reaction and results are consistent with literature reporting experimentally measured ignition temperatures.

The exothermic surface chemistry associated with the alumina passivation shell surrounding aluminum (Al) particles and fluorine from fluoropolymer materials is investigated. In particular, polytetrafluoroethylene (PTFE) has been synthesized with varying chain lengths and combined with nanometric Al fuel particles. The Al-PTFE kinetics were analyzed using equilibrium diagnostics including differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) for calorific and phase change behavior coupled with additional flame speed measurements. The objective was to understand the effects of varying PTFE molecular structure on the kinetic and energy propagation behaviors of these composites. Results showed a pre-ignition reaction (PIR) with longer chained PTFE samples and not with the shorter chained PTFE samples. The PIR is attributed to fluorine dislodging hydroxyls from the alumina (Al₂O₃) passivation surface and forming Al-F structures. Composites exhibiting the PIR correspondingly result in significantly higher flame speeds. The PIR surface chemistry may contribute to promoting the melt dispersion mechanism (MDM) responsible for propagating energy in nano Al reactions. Composites with a PIR also have higher heats of combustion in both the PIR and main reaction exotherms. These results help elucidate the influence of molecular scale surface chemistry on macroscopic energy propagation.

A pre-ignition reaction (PIR) once thought to be unique to aluminum (Al) and fluorine based oxidizer reactions are observed for aluminum and an iodine containing oxidizer. This pre-ignition reaction is exothermic and precedes the main exothermic reaction corresponding to aluminum combustion. For the aluminum and iodine oxide system, exothermic surface chemistry was recently predicted for I-O fragments forming bridge bonds with the alumina passivation shell using first principle calculations, but now has been observed experimentally. Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TG) were used to assess aluminum and iodine pentoxide (I₂O₅) powder mixtures. Various equivalence ratios were examined and found to affect the PIR onset temperature. Prior to this work, the PIR was attributed solely to surface reactions of the halogen with the Al₂O₃ surface; but, results shown here indicate both the alumina surface and aluminum core contribute to a PIR and a minimum activation energy is necessary for PIR production. Lead Students on these projects: Cory Farley (PhD, now at LANL), Oliver Mulamba (PhD, now at West Texas A&M as Assistant Professor)

b. Synthesis and characterization of fluoropolymer coated aluminum particles

Four different synthesis strategies were pursued to understand the affect fluorine has on aluminum combustion. (i) The first synthesis method coated aluminum fuel particles using a wet chemistry approach with a fluoropolymer acid. (ii) The second embedded these coated particles into epoxy binders via electrospinning. The motivation of the second approach was to advance the science of 3D printing of energetic materials (additive manufacturing) which much start by embedding energetics into a printable fluoropolymer. (iii) The third approach used a doctor blade to draw a fluoropolymer-fuel particle slurry into thin films or sheets of energetic materials. This is a simplistic approach to creating highly dense solid films of reactive materials. (iv) The final approach coated composite energetic mixtures with various fluoropolymers to assess the hydrophobicity of these coatings and the energetic behavior of the material submerged underwater.

i. Coating Al particles with fluoropolymer

Thermal equilibrium and flame propagation experiments were performed for three thermites each containing 80 nm average diameter Al particles combined with MoO3. Two thermites contained Al coated particles with different acids and an uncoated Al thermite was used as a baseline for comparison. The acids were self-assembled monolayers of perfluorotetradecanoic acid (PFTD) and perfluoro sebacic acid (PFS) such that the thermites were labeled: Al-PFTD/MoO3, Al-PFS/MoO3 and Al/MoO3. Results showed that Al-PFTD/MoO3 had the highest velocity and almost double that of Al/MoO3. On the other hand, Al-PFS/MoO3 had the lowest velocity and only 48% as high as Al/MoO3. Equilibrium analyses revealed that the PFTD acid promoted a lower onset for a pre-ignition reaction which may be spurred by reduced structural stability of the acid molecular chain (i.e., more sterically hindered). The lower onset for the fluorine aluminum pre-ignition reaction was a significant difference in the heat flow trends for the two different acid coatings and may be an indication of a key

Schematics of surface functionalized Al particles with two different acids: perfluorotetradecanoic acid (PFTD) and perfluoro sebacic acid (PFS).
parameter controlling reactivity of the acid coated Al. Activation energy (Ea) showed an inverse trend with velocity, with highest velocity associated with the lowest Ea. This finding was anticipated because propagation velocity can be described as a series of ignition sites such that lower activation energy correlates with higher propagation velocity for the similar thermites examined here.

These findings are impactful because they suggest that the structure of the acid coating can be tailored to enhance or reduce the reactivity of the thermite. Results suggest that because the perfluorotetradecanoic acid (PFTD) coating is less stable and contains a higher concentration of fluorine, these factors promote an earlier onset of a pre-ignition reaction that enhances thermite reactivity (in terms of higher velocity and lower activation energy). On the other hand, perfluoro sebacic acid (PFS) is more stable, requires greater bond energy for dissociation and results in a delayed onset for the PIR, higher activation energy and lower flame speeds; reducing the overall thermite reactivity. (Lead Student: Keerti Kappagantula)


**ii. Advancing additive manufacturing science for energetic material synthesis**

Polystyrene fibers loaded with an energetic blend of nanoaluminum (n-Al) and perfluoropolyether (PFPE) were successfully fabricated via electrospinning producing a nanothermite energetic material. Fibers were generated with loadings from 6 up to 17 wt% n-Al/PFPE incorporated into the fiber. Microscopy analysis by SEM and TEM confirm a uniform dispersion of PFPE treated n-Al on the outside and inside of the fibers. Metalized fibers were thermally active upon immediate ignition from a controlled flame source. Thermal analysis by differential scanning calorimetry (DSC) found no change in glass transition temperature when comparing pure polystyrene fibers with fibers loaded up to 17 wt% n-Al/PFPE. Thermal gravimetric analysis (TGA) revealed a shift in decomposition temperatures to lower onsets upon increased loadings of n-Al/PFPE blends.
consistent with previous studies. Flame propagation studies confirmed that the metallized fibers are pyrolants. These metallized fibers are a recent development in metastable intermolecular composites (MICs) and details of their synthesis, characterization, and thermal properties are presented.

An operationally simple blendable approach to producing structural energetic composites loaded with nanoaluminum (n-Al) particles coated by perfluoropolyethers (PFPE) yields shape moldable, structurally flexible materials. The epoxide system of poly(ethylene glycol) diglycidyl ether (PEG-DGE) and triethylenetetramine (TETA) are partially cured with an energetic blend of n-Al/PFPE core/shell particles and mechanically mixed and produce a homogeneous composite material whereby energetic potency is indefinitely shelf-stable. The composites are characterized by a suite of thermal techniques using DSC, TGA, and SDT in addition to open flame burn rate and heat of combustion measurements. This composite system may further expand the use of energetic materials with tailorable exothermic properties. (Lead Student: Keerti Kappagantula)


### iii. Thin film thermite synthesis

A new method for synthesis of thin energetic films based on doctor blade casting has been developed. The method requires powdered reactants such as Mg-MnO2 to be prepared with a solvent-binder system and three systems were investigated here. Thickness measurements show that Mg-MnO2 coatings prepared using NMP-PVDF were consistently thinner and smoother than coatings cast with acetone-Viton or xylene-paraffin at comparable binder concentrations. The Mg-MnO2-PVDF formulation was determined to be most effective for preparation as a thin film coating based on greater homogeneity of the mixture and smoother surface roughness. Increasing the PVDF concentrations in Mg-MnO2-PVDF resulted in higher heats of combustion that may be due to an increase in available oxidizer from the PVDF. With increasing binder concentration, flame velocities decreased despite increased calorific outputs. This trend is attributed to lower thermal conductivity of the binder. Overall, the effect of the lower thermal conductivity on

![SEM and EDS cross section image of Viton based suspension at 40% solids and 1% Viton. Distribution of Mg-MnO2 is consistent with well mixed deposition and shows no evidence of settling.](image)
flame velocity counterbalances the increase in chemical energy available for propagation. Confinement greatly increases flame velocity even for these low gas generating films. The Mg-MnO2-PVDF flame velocity increased by an order of magnitude (i.e., from 100 to 3000 cm/s) for open versus confined flame velocity tests, respectively. This may be due to a shift in transport mechanism from conduction to convection. The flame front emits hot particulate matter which, in the presence of confinement, is directionized. The formation of hot gaseous products has less effect in open tests. However, in confined tests, these gaseous products result in a pressure wave that propels the advected flame front faster. If not fully confined, these gases escape and result in a slower flame front. (lead student: Kelsey Meeks)


(iv) Hydrophobic coatings on energetic formulations

Water-repellent nano-coatings for submerged combustion of nano-energetic composite materials were developed. These coatings may have applications for oceanic power generation, underwater ordnance, propulsion, metal cutting, and torch technologies. Nano-coatings were deposited on thermite pellets by a vapor-phase technique. Two types of deposition techniques studied were chemical vapor deposition (CVD) and atomic layer deposition (ALD). A total of six types of nano-coatings were applied on the thermite pellets. Various process parameters to produce the coatings were explored. Characterization of the nano-coatings was carried out using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and contact angle goniometry. Submerged combustion tests of the nano-coated thermite pellets were performed as a function of submerged time. The pellets were submerged in de-ionized water for 3, 5, and 10 days. The energy released by the thermite reaction was analyzed and compared to other types of nano-coated pellets. Initial results of a fluorocarbon self-assembled monolayer (FSAM) coating were compared with an ALD coating composed of Al2O3. Results show that with increasing submerged time, there was a decrease in the ratio of bubble energy to total energy of combustion (Kc=K_bubble/K_combustion) for all coatings tested. The initial bubble energy of the pellets coated with FSAM and ALD with Al2O3 was 133.3 and 142.2 (KJ/Kg), respectively. After submersion for 10 days, the bubble energy reduced to 10.4 and 15.6 (KJ/Kg), respectively. The value of Kc for the FSAM coating decreased by a factor of 12.8 whereas the ALD with Al2O3 coating decreased by a factor of 9.1. The hydrophobic coating is critical for energy generation because without it, the pellets do not ignite, resulting in 100% loss of energy. (Lead Students: Eric Collins and Eric Nixon)


(3) Diagnostic Developments

Experimental research studying energetic material combustion often requires instrumentation that is uniquely designed and cannot be purchased from a company. As our work evolves, so does the need to advanced diagnostics. One focus has been on resolving 2D transient
temperatures. Towards this end we have coupled our existing pyrometer with a high speed IR camera to resolve two dimensional spatial distributions of temperature from a reacting thermite as a function of time. The following two paragraphs describe this diagnostic in more depth. Lastly, our early collaborations with Aberdeen Proving Ground have transitioned a heat flux sensor into application. This sensor was developed to quantify the heat flux from an energetic material spray onto a substrate. The final two paragraphs describe this diagnostic in more depth.

a. Two dimensional temperature mapping

Existing temperature measurement techniques for combustion reactions were reviewed. Although the current methods facilitate temperature measurement for one location, there are no available techniques to determine a comprehensive temperature field encompassing an entire reaction. A unique method for determining the spatial distribution of temperature during combustion of composite metal materials (CMMs) was developed by integrating multi wavelength radiometry with thermal imaging techniques. A five channel radiometer was used to determine the maximum temperature of CMM reactions and this point source measurement corresponds well with previously published values. Specifically, reaction temperatures for Al/MoO₃, Al/Fe₂O₃ and Al/CuO were measured using the radiometer and are within 10% of reported values. This point source temperature was then coupled with irradiance measurements from an IR camera that provides data for a 3.5 cm by 8 cm field consisting of 120x256 pixels. The emissivity of the reaction was determined by integrating the temperature reading from the radiometer with black body calibration data for the IR camera. The temperature of every location of the thermal image for the Al/PTFE reaction was then determined by combining the emissivity of the reaction with the radiance values obtained from the IR camera software. The result is a detailed thermal map of a large field of interest that shows temperature gradients associated with a reaction.

A unique method for characterizing the temperature fields during the combustion of fast moving energetic materials was developed. Thermal images of Al/PTFE and Al/CuO with and without additives were obtained at the point of time when the reactions reach their maximum temperature. The temperatures were measured using a five channel multi wavelength radiometer coupled with an IR camera. Thermal images show two distinct temperature zones: a hot zone surrounding the point of ignition where the highest temperatures ($T_{max}$) were recorded and an intermediate zone, with temperatures lower than those seen in hot zone but much greater than room temperature. Temperature changes along the vertical axis passing through the point of highest temperature were plotted as a function of distance from the point of ignition such that inflection points identifying temperature gradients can be measured to provide an indication of the range of the thermal influence of the reaction.

Still frame image of the Al/PTFE reaction at instant the reaction reaches $T_{max}$ and the spatial distribution of temperature at that instant. The contour thresholds are presented at 500 degree gradients but could be adjusted to improve resolution, as desired. Blue shading indicates $T<750K$ and red shading indicates $T>2500K$. The point location (i.e. corresponding to the radiometer measurement of $T_{max}$) is noted and the maximum temperature is labeled.
For Al/CuO, additives with higher heats of combustion like B and Mg increase the maximum temperatures in the hot zone. It was also seen that the faster the reactions attain $T_{max}$ (Al/CuO/B and Al/CuO/Mg), the more extensive the temperature fields generated due to the momentum of the gaseous and condensed phase products, which are ejected farther from the hot zone. This increased the thermal field effects in the far-field regions significantly and shifted the inflection points much farther than the slower moving reactions. Additives like Fe and Mn, produced lower $T_{max}$ and did not react with CuO but showed improved far-field temperatures and farther inflection points as they were more successful in propagating energy from the hot region. Reactions generating more gaseous combustion products like Al/PTFE had increased far-field temperatures and thus farther inflection points compared to reaction that generated less gas like Al/CuO. In addition to the condensed phase products, it was also seen that the gases carried the energy from the hot zone effectively into the far-field. In conclusion, temperature fields are controlled by the introduction of different additives that optimize specific energy transport mechanisms such as overall calorific output coupled with multiphase convection.


b. Heat flux sensor

Temperature measurements and heat flux values were determined for thermite sprays impingent on a surface. The surfaces were positioned between 1.27 and 3.81 cm (0.5 and 1.5 in) from the spray nozzle for Al + CuO, Al + MoO$_3$, and Al + Fe$_2$O$_3$ sprays. The maximum temperature and heat flux were located close to the nozzle and decreased as the sensor moved outward. A heat flux threshold of 4550 W/cm$^2$ was found to cause damage to a silicon substrate surface. Two interesting observations were made in this experiment. First, the Al+Fe$_2$O$_3$ reaction caused damage to the substrate at all standoff distances which is a result of very low gas generation, producing a more focused condensed phase spray. SEM images evidenced craters indicating particle impact and penetration. Second, the Al + CuO and Al + MoO$_3$ only caused damage to the substrate when positioned very close to the nozzle which may be attributed to heat flux values above the damage threshold but may not be a result of particle impact and penetration as no observations of crater indentations on the surface were observed. The higher gas generation properties of these two reactions result in a more dispersed, less focused spray and lower heat flux values further from the nozzle. These results elucidate the roles of thermal and physical properties such as heat flux and gas generation on the transfer of energy from a reacting thermite spray to a substrate.

(4) Modeling and Theoretical Development of Aluminum Particle Reaction Mechanisms

Two aspects of modeling have been the focus over this period. The first was developing the theory of the melt dispersion mechanism. According to this theory, the ratio of the core to shell of an aluminum particle is a key parameter promoting the bursting and dispersion of aluminum in a nanoaluminum particle. Towards this end, our group synthesized aluminum particles with varied core-shell structures by thermally growing the alumina shell on 90 nm diameter Al particles. In this way, the overall diameter of the particles did not change, but the shell thickness was shown to grow from about 2 nm to nearly 10 nm thick. Also, the products from a reaction considered to undergo the melt dispersion mechanism were analyzed using SEM. The images reveal evidence of particle size predicted to be produced by the MDM. Both of these studies are highlighted in more depth below. Following this discussion, further analysis of reactivity on a single particle scale was performed as well as an analysis of detonation behavior of loose powder reactions. These are also discussed in more detail below.

a. Melt Dispersion Mechanism

Flame propagation rates for nanometric particle composites of aluminum (Al) and molybdenum trioxide (MoO₃) were examined. The Al particles were prepared by thermally treating the particles at 480°C for time increments up to 180 minutes in oxygen and 90 minutes in argon. This treatment caused the aluminum passivation shell to grow and there is also evidence of shell damage due to treatment. Results reveal several interesting behaviors: flame speeds initially on the order of several hundred meters per second were reduced with damage to the oxide shell, and there is a weak dependence of the flame speed on the ratio of particle radius to shell thickness (M) in the range 6.1 < M < 13.4. The sharp drop in flame rate at further reduction in M down to 5.0 is consistent with a similar drop observed for adding alumina to the reactive mixture. All observations are consistent with the melt dispersion mechanism associated with Al nanoparticle oxidation.

![TEM Images](initial.png)

Synthesis of aluminum particles with controlled shell structure for accelerated oxidation. A. TEM of 120 nm Al particle (untreated); B. TEM of shell from particle in A., note the shell thickness of 3.87 nm; and, C. TEM of Al particle (179 nm diameter) treated thermally (480°C) and chemically (fluorine controlled environment) for 60 minutes, note the shell thickness of 5.84 nm. M is the ratio of particle core radius to shell thickness.

Flame propagation studies for Al nanoparticles (80 nm) and micron particles (3-4.5 μm) mixed with MoO₃ in both an open and confined burn setup were examined. A scanning electron microscopy (SEM) analysis of the reactants and products reveals quantitative size data that
contributes toward an understanding of the governing reaction mechanism for these reactions. For the confined burn tube experiments, nanoscaled reactants exhibited a flame speed of 960 m/s, the same as has been reported in previous experiments. Micron scale particles exhibited a flame speed of 402 m/s, much higher than the 244 m/s obtained previously for 1-3 µm particles. These flame speeds are in quantitative agreement with predictions based on the recently developed melt-dispersion mechanism (MDM) describing the reaction of Al particles. It also demonstrates that some micron particles can reach flame speeds just 42% lower than the fastest nanoparticles, while micron scale particles are less expensive and do not have the pre-combustion safety and environmental issues typical of nanoparticles. The SEM analysis reveals a significant (at least by factor of 3.7 for nanoparticles) reduction in Al particle size post combustion, which is in agreement with the MDM and in contrast to the predictions based on diffusion mechanisms. Open burn experiments with nanoscale reactants have flame speeds of 12 m/s and product particle sizes almost as small as those in the burn tube experiments. However, the presence of some large particles, which may grow based on the diffusion mechanism, exclude evaporation and the homogenous nucleation mechanism. For open burn experiments with micron reactants, with flame speeds of 9 m/s, SEM analysis shows a molten-resolidified product with no distinguishable particles and cavities containing numerous nanoparticles with a measured diameter of 36 nm.


**b. Modeling of powder media reactions**

The combustion of nanometric aluminum (Al) powder with an oxidizer such as molybdenum trioxide (MoO₃) is studied analytically. The analysis was performed to correlate individual Al particle gasification rates to macroscopic flame propagation rates observed in flame tube experiments. Examination of various characteristic times relevant to propagation of a deflagration reveals that particles below about 1.7 nm in diameter evaporate before appreciable chemical reactions occur. Experimental studies use Al particles greater than 1.7 nm in diameter such that a diffusion flame model was developed to better understand the combustion dynamics of multiphase Al particles greater than 1.7 nm diameter relative to experimentally measured macroscopic flame propagation rates. The diffusion flame model predicted orders of magnitude slower propagation rates than experimentally observed. These results imply that (1) another reaction mechanism is responsible for promoting reaction propagation and/or (2) modes other than diffusion play a more dominant role in flame propagation.

The evaporation and combustion of nanometric aluminum particles with an oxidizer such as MoO₃ is analyzed. Characteristic times are evaluated to estimate droplet diameters small enough such that Al vaporization precedes combustion using both continuum and free molecular theories. The results showed that it is unlikely that droplets will fully evaporate before reacting in the gas phase. A droplet evaporation and combustion model was further applied to quantify single droplet reaction velocities in comparison to the bulk flame propagation measurements observed in the literature. The model showed a 100 nm Al droplet produces flame speeds on the order of 0.9 m/s and two orders of magnitude less for the flame spread through bulk media. This
result implies that diffusive (Random Walk) flame spread is not fast enough to propel the reaction front in bulk media to the observed levels of $10^2$-$10^4$ m/s. Other factors that may contribute to the high measured propagation rates may include the added influences of convective or radiative modes of energy propagation, or perhaps modeling the reaction as a detonation rather than a diffusive deflagration may be more appropriate.

Examining the Al-MoO$_3$ flame propagation measurements in semi-confined flame tubes from the perspective of a detonation model was the approach employed here. This analytical study showed a strong dependence of packing density (expressed in terms of theoretical maximum density percentage (TMD%)) on the equilibrium sound speed. For example, sound speed can range from 80 to 350 m/s for multiphase product species for densities decreasing from 20% TMD. In contrast, frozen gas particle mixture sound speeds were not shown to be consistent with experiential data. Using the equilibrium sound speed, detonation velocities were determined for various heats of combustion and correlate well with experimental observations of propagation velocity and the trend of decreasing velocity with increasing TMD%.

This work could be extended, e.g., by consideration of the effects of nonequilibrium products, gas evolution in the products, and the detailed structure of the detonation wave. For example, it is possible that slow chemical reactions or phase changes could be present, leading to products that are different from the products assumed to apply in this research. It is also of interest to investigate factors such as finite-rate chemical kinetics and phase changes, radiant heat transfer effects, and energy and momentum transfer between phases. This would lead to a better understanding of the controlling physics of detonation waves in nanoscale media.


**Conclusion**

The research covering this period has led to advancements in our understanding of energy transport within particulate media spurred by a variety of ignition sources, reaction kinetics that are the key to advancing synthesis strategies and diagnostics that will empower future research. Over 30 archival journal publications have been produced that are highly cited in high impact journals. Future efforts will examine surface chemistry and reactivity associated with aluminum fuel particles as well as mechanical properties that influence their reactivity. All students supported on this work were US citizens and have gone on to work in military or national laboratories, US industry, or academia, and all live and work in the USA.
Technology Transfer

We have had several interactions with industry, military and national laboratories throughout this project duration. Individual are highlighted below and further explanation is provided.

- Drs. Berry Homan, Kevin Mc Nesby, Brad Forch (APG, ARL)
- Drs. Stephen Howard, Richard Beyer, Eric Collins (APG, ARL)
- Dr. Luke Currano (Adelphi, ARL)
- Drs. Jillian Horn, Rebecca Wilson, Jason Jouet (Indian Head NSWC)
- Dr. Benjamin Shaw (UCDavis)
- Drs. Eric Steffler, Michael Daniels (INL)
- Dr. Valery Levitas (Iowa State University)
- Drs. John Granier and Dennis Wilson (EMPInc.)
- Dr. Kurt Schroder, NovaCentrix
- Mr. Bryan Bockmon (Rocky Mountain Scientific Lab)
- Dr. Emily Hunt (West Texas A&M)
- Dr. David Irvin (Systems & Materials Research Corp)
- Drs. Cory Farley & Charles Crane (LANL)
- Dr. Santanu Chadhuri (WSU)
- Dr. Scott Iacono (Air Force Academy)
- Drs. Christopher Apblett & Shawn Stacy (Sandia National Lab)
- Drs. Andreas Neuber, Jordan Berg (Texas Tech)
- Drs. Alex Gash and Kyle Sullivan (LLNL)

Some highlights are as follows.

Within industry, we are working closely with Dr. Kurt Schroder and many others from NovaCentrix in Austin, Texas. Specifically our working relationship involves identifying synthesis routes to prepare nano-Al particles for research by tailoring certain parameters of the aluminum particles. We then use these materials to experimentally examine reaction mechanisms.

Our lab characterizes the combustion behaviors of new formulations of energetic materials. Towards this end, much of our technology transfer has been in developing an understanding of combustion dynamics of materials synthesized by other labs. For example, Lawrence Livermore National Laboratory is developing sol-gel chemistry as a synthesis technique for nanocomposite mixtures. Specifically, Dr. Alex Gash works with us and synthesizes nano-particles of NiO and MnO2 using sol-gel chemistry. Our laboratory characterized the combustion behaviors of these mixtures which allowed the LLNL group to refine the synthesis technique. Similarly, we are working with Indian Head Naval Surface Warfare Center, specifically Dr. Rebecca Wilson and Jillian Horn, to characterize their synthesized coated aluminum particles. Also, Dr. David Irvin from industry (SMRC) is a chemist that has been developing surfactants to aid in dispersion of solid fuel particles and we characterize the reactivity of their materials.

We are also actively working with the Army Research Laboratory and Drs. Richard Beyer and Berrie Homan. We are working with all of these individuals to transition our findings into applications (such as the heat flux sensor now housed at APG).
We work with Dr. John Granier from EMPI to characterize the reactivity of small scale samples, specifically focusing on reaction kinetics. This work helps them understand their large scale blast experiments and design formulations accordingly.

We work with theoreticians, such as Drs. Valery Levitas, Santanu Chadhuri, Ben Shaw. Both have developed theories to explain aluminum reactivity and we have supplemented their models with purposefully designed experimental confirmations.