

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY) 14-12-2010		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Jun-2004 - 31-Dec-2010	
4. TITLE AND SUBTITLE Final Report: Combustion and Ignition Studies of Nanocomposite Energetic Materials			5a. CONTRACT NUMBER W911NF-04-1-0217		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611103		
6. AUTHORS Michelle L. Pantoya			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Texas Technical University 203 Holden Hall Box 41035 Lubbock, TX 79409 -1035			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 45696-EG-PCS.24		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT This final report summarizes the major contributions to the basic science of nanocomposite reactive materials and focuses on fundamental ignition and energy propagation behaviors. Nanometric aluminum (Al) fuel particles were examined with a variety of oxidizers including metals, metal oxides, halogens, and polymer binders. Some work was also pursued on other fuels such as boron (B) and manganese (Mn). New diagnostics were developed to resolve equilibrium as well as non-equilibrium reaction kinetics. These include new imaging diagnostics to resolve					
15. SUBJECT TERMS Energetic Material Combustion, nanoparticles, thermites, reactive materials, high speed IR diagnostics, flame propagation, energy transfer, laser ignition, flame spreading					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Michelle Pantoya
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 806-742-3563

Report Title

Final Report: Combustion and Ignition Studies of Nanocomposite Energetic Materials

ABSTRACT

This final report summarizes the major contributions to the basic science of nanocomposite reactive materials and focuses on fundamental ignition and energy propagation behaviors. Nanometric aluminum (Al) fuel particles were examined with a variety of oxidizers including metals, metal oxides, halogens, and polymer binders. Some work was also pursued on other fuels such as boron (B) and manganese (Mn). New diagnostics were developed to resolve equilibrium as well as non-equilibrium reaction kinetics. These include new imaging diagnostics to resolve surface reaction through highly luminescent flames, new sensors to monitor heat flux and temperature from the hostile energetic material environments during reaction, as well as equilibrium diagnostics that resolve fundamental thermal properties of reactant formulations and differential thermal analysis techniques that enable identification of gas phase species. Results have shown (1) dramatically increased ignition sensitivity of nanometric Al particles; (2) enhanced energy release rates for fast heating ignition conditions; (3) new models that describe the mechano-chemical reactive behavior unique to nanoparticles; (4) new synthesis approaches that take advantage of reactive behaviors associated with nano-particles. Technology developed under this project is being transferred to our military collaborators in an effort to integrate these diagnostics into applications that exploit the benefits of nano-particle combustion.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

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

1. "Non-Uniform Laser Ignition in Energetic Materials," J. Granier, T. Mullen and M. L. Pantoya, *Combustion Science and Technology* 175(11), 1929-1951, (2003).
2. "The Effect of Size Distribution on Burn Rate in Nanocomposite Thermites: A Probability Density Function Study," J. J. Granier and M. L. Pantoya, *Combustion Theory and Modelling* 8(3), 555-565 (2004).
3. "The Role of the Al₂O₃ Passivation Shell Surrounding Nano-Aluminum Particles in the Combustion Synthesis of NiAl," J. J. Granier, K. B. Plantier and M. L. Pantoya, *Journal of Materials Science* 39(21), 6421-6431 (2004).
4. "Nickel Aluminum Superalloys Created by the Self-propagating High-temperature Synthesis (SHS) of Nano-particle Reactants," E. M. Hunt, J. J. Granier, K. B. Plantier and M. L. Pantoya, *Journal of Materials Research* 19(10), 3028-3036 (2004).
5. "Nano-scale Reactants in the Self-Propagating High-Temperature Synthesis of Nickel Aluminide," E. Hunt, K. Plantier, M. Pantoya, *Acta Materialia* 52(11), 3183-3191 (2004).
6. "Laser Ignition of Nanocomposite Thermites," J. Granier and M. Pantoya, *Combustion and Flame* 138(4), 373-383 (2004) [DOI: 10.1016/j.combustflame.2004.05.006].
7. "The Effect of Nanocomposite Synthesis on the Combustion Performance of a Ternary Thermite" D. Prentice, M. L. Pantoya, B. Clapsaddle, *Journal of Physical Chemistry B* 109(43), 20180-20185 (2005).
8. "Ignition Dynamics and Activation Energies of Metallic Thermites: From Nano- to Micron-scale Particulate Composites," E. M. Hunt and M. L. Pantoya, *Journal of Applied Physics* 98(3), 034909 (2005). [DOI:10.1016/j.combustflame.2004.10.009]
9. "Combustion Wave Speeds of Nanocomposite Al/Fe₂O₃: The Effects of Fe₂O₃ Particle Synthesis Technique," K. B. Plantier, M. L. Pantoya and A. E. Gash, *Combustion and Flame* 140(4), 299-309 (2005) [DOI: 10.1016/j.combustflame.2004.10.009].
10. "Combustion Velocities and Propagation Mechanisms of Meta-stable Intermolecular Composites," B. S. Bockmon, M. L. Pantoya, S. F. Son, B. W. Asay, J. T. Mang, *Journal of Applied Physics* 98(6), 064903 (2005) [DOI: 10.1063/1.2058175].
11. "Combustion Behaviors of Highly Energetic Thermites: Nano versus Micron Composites," M. L. Pantoya and J. J. Granier, *Propellants, Explosives, Pyrotechnics* 30(1), 53-62 (2005) [DOI: 10.1002/200400085].
12. "Dependence of size and size distribution on reactivity of aluminum nanoparticles in reactions with oxygen and MoO₃," J. Sun, M. L. Pantoya, and S. L. Simon, *Thermochimica Acta* 444(2), 117-127 (2006). [DOI: 10.1016/j.tca.2006.03.001]
13. "Combustion Synthesis of Metallic Foams from Nanocomposite Reactants," E. M. Hunt, M. L. Pantoya and R. J. Jouet, *Intermetallics* 14 (6), 620-629 (2006).
14. "The Effect of Slow Heating Rates on the Reaction Mechanisms of Nano and Micron Composite Thermite Reactions," J. J. Granier and M. L. Pantoya, *Journal of Thermal Analysis and Calorimetry* 85(1), 37-43 (2006).
15. "Combustion Effects of Environmentally Altered Molybdenum Trioxide Nanocomposites," K. Moore and M. L. Pantoya, *Propellants Explosives Pyrotechnics* 31(3), 182-187 (2006).
16. "Combustion Behaviors Resulting from Bimodal Aluminum Size Distributions in Thermites," K. Moore, M. L. Pantoya, and S. F. Son, *Journal of Propulsion and Power* 23(1), 181-185 (2007). [DOI: 10.2514/1.20754]
17. "Melt Dispersion Mechanism for Fast Reaction of Nanothermites," Levitas, V. I., Asay, B. W., Son, S. F., and Pantoya, M. L., *Applied Physics Letters* 89(7), 071909 (2006). [DOI: 10.1063/1.2335362] (Reprod. in *Virtual J. Nanoscale Sci. & Techn.*, 2006, Aug. 28)
18. "A New Mechanism for Formation of Spatial Oscillations in SHS of Ni/Al Bilayer Foils," E. B. K. Washington, D. Aurongzeb, J. M. Berg, D. Osborne, M. Holtz, M. Pantoya, H. Temkin *International Journal of SHS* 15(2), 121-132 (2006).
19. "Combustion Wave Speeds of Sol-gel Synthesized Tungsten Trioxide and Nano-Aluminum: The Effect of Impurities on Flame Propagation," D. Prentice, M. L. Pantoya, and A. E. Gash, *Energy & Fuels* 20(6), 2370-2376 (2006). [DOI:10.1021/ef060210i].
20. "Effect of Aluminum Particle Size on the Thermal Degradation of Al/Teflon Mixtures," D. T. Osborne and M. L. Pantoya, *Combustion Science and Technology* 179(8), 1467-1480 (2007). [DOI: 10.1080/00102200601182333]
21. "Mechanochemical Mechanism for Fast Reaction of Metastable Intermolecular Composites Based on Dispersion of Liquid Metal," V. I. Levitas, B. W. Asay, S. F. Son and M. L. Pantoya, *Journal of Applied Physics* 101(8), 083524 (2007). [DOI: 10.1063/1.2720182]
22. "The Effect Of Aluminum On The Heat Flux From A Simulated Rocket Propellant Flame," R. B. White, S. W. Dean, M. L. Pantoya, D. A. Hirschfeld, W. Gill and W. W. Erikson, *Journal of Propulsion and Power* 23(6), 1255-1262 (2007). [DOI: 10.2514/1.28161].
23. "Small Angle X-ray Scattering Analysis of the Effect of Cold Compaction of Al/MoO₃ Thermite Composites," J. A. Hammons, W. Wang, J. Ilavsky, M. L. Pantoya, B. L. Weeks and M. W. Vaughn, *Physical Chemistry Chemical Physics* 10, 193-199 (2008). [DOI:10.1039/b711456g]
24. "Characterization of a gas burner to simulate a propellant flame and evaluate aluminum particle combustion," M. Jackson, M. L. Pantoya and W. Gill, *Combustion and Flame* 153(1-2), 58-70 (2008). [DOI:10.1016/j.combustflame.2007.11.014]
25. "Melt-Dispersion versus Diffusive Oxidation Mechanism for Aluminum Nanoparticles: Critical Experiments and Controlling Parameters," V. I. Levitas, Pantoya, M. L., B. Dikici, *Applied Physics Letters* 92(1), 0011921 (2008). [DOI:10.1063/1.2824392]
26. "Melt-dispersion mechanism for fast reaction of aluminum particles: Extension for micron scale particles and fluorination," Levitas, V. I., Pantoya, M. L.; Watson, K. W. *Applied Physics Letters*, v 92, n 20, 2008, p 201917
27. V.I. Levitas and M.L. Pantoya, "Mechanochemical Mechanism for Fast Reaction of Metastable Intermolecular Composites Based on Dispersion of Liquid Metal, *International Journal of Energetic Materials and Chemical Propulsion* 7(1), 2008.
28. "Fast reactions with nano and micron aluminum: a study on oxidation versus fluorination," K.W. Watson, M. L. Pantoya, V. I. Levitas,

Combustion and Flame 155(4); 619-634 (2008).

29. "A Multi-Objective Modeling Approach for Energetic Material Evaluation Decisions," M. J. Schniederjans, M. L. Pantoya, J. J. Hoffmann, and D. L. Willauer, *European Journal of Operational Research*, V. 194, n 3, May 1, 2009, 629-636.
30. "The effect of bulk density on the reaction dynamics in nano and micron particulate thermites," M. L. Pantoya, V. I. Levitas, J. J. Granier, J. B. Henderson, *Journal of Propulsion and Power* 25(2); March-April (2009).
31. "Impact Ignition of nano and micron composite energetic materials," A. Hunt, A. Purl, E.M. Hunt and M.L. Pantoya, *International Journal of Impact Engineering*, v36 n 6, p842-846 (2009).
32. "The influence of alumina passivation on nano-Al/Teflon reactions," S.W. Dean and M.L. Pantoya, *Thermochimica Acta* 493(1-2), p 109-110 (2009).
33. "The Influence of Aluminum Passivation on the Reaction Mechanism: Flame Propagation Studies", B. Dikici, M.L. Pantoya, Levitas, V., R.J. Jouet, *Energy & Fuels* 23, p4231-4235 (2009).
34. "Aluminum Fueled Nanocomposites for Underwater Reaction Propagation," S.C. Stacy, M.L. Pantoya, D.J. Prentice, M.A. Daniels, E.D Steffler, *Advanced Materials and Processes* 167(10) p 33-35, Aug 2009 [DOI: 10.1361/amp16710p33].
35. "Effect of the alumina shell on the melting temperature depression for nano-aluminum particles," V.I. Levitas, M.L. Pantoya, G. Chauhan, and I. Rivero, *Journal of Physical Chemistry C*, 113(2), p 14088-14096, 2009.
36. A Diagnostic for Quantifying Heat Flux from a Thermite Spray, EP Nixon, ML Pantoya, DJ Prentice, ED Steffler, MA Daniels, and SP D'Arche, *Measurement Science and Technology*, 21: 025202; 2010.
37. M. Pantoya and E. Hunt, *Nanochargers: Energetic Materials for Energy Storage*, *Applied Physics Letters* 95; 253101 (2009). (Reprod. in *Virtual J. Nanoscale Sci. & Techn.*, 21(2) 2010, Jan. 11.
38. S.W. Dean, M.L. Pantoya, A.E. Gash, S.C. Stacy, L. Hope-Weeks, "Enhanced Convective Heat Transfer from Non-gas Generating Nanoscale Thermite Reactions," *Journal of Heat Transfer* 132(11), 2010; DOI: 10.1115/1.4001933.
39. B. Dikici, M.L. Pantoya, V. Levitas, *The Effect of Pre-heating on Flame Propagation Behavior in Nanocomposite Thermites*, *Combustion and Flame*, v157(8); 1581-1585 (2010).
40. C. Farley and M.L. Pantoya, *Reaction Kinetics of Nanometric Aluminum and Iodine Pentoxide*, *Journal of Thermal Analysis and Calorimetry* 102(2), 609-613 (2010) DOI: 10.1007/s10973-010-0915-5.
41. E. M. Hunt and M. L. Pantoya, *Impact Sensitivity of Intermetallic Nanocomposites: A Study on Compositional and Bulk Density*, *Intermetallics*, v18(8); 1612-1616 (2010).
42. Charles A. Crane, Michelle L. Pantoya, Jerry Dunn, "Evaluating Energy Transfer from Energetic Materials to Steel Substrates," *International Journal of Thermal Science* 49(10) 1877-1885, 2010.

Number of Papers published in peer-reviewed journals: 42.00

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

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

1. S.Datta, M.L. Pantoya, "Reaction Dynamics of Aluminum-Viton-Acetone Droplets," 18th International Conference on Composites or Nano Engineering, Anchorage, AK, July 2010.
2. S.Datta, M.L. Pantoya, B. Dikici, S. Ekwari, "Reaction Dynamics and Probability Study of Aluminum-Viton-Acetone Droplets," 46th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, Nashville, TN, July 2010.
3. Eric Nixon, Eric Collins, Charles Crane, and Michelle Pantoya, "Reaction Dynamics of a Thermite Spray Gun" 2010 Spring Technical Meeting/The Central States Section of the Combustion Institute, Champaign IL, March 21-23, 2010.
4. Dikici B., Pantoya M.L., Shaw B.D. "Analysis of the Influence of Nanometric Aluminum Vaporization on Flame Propagation in Bulk Powder", Paper Number AIAA-2010-1598, 48th AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition, 4-7 January 2010, Orlando, Florida.
5. Dikici B., Pantoya M.L., "The influence of Aluminum Passivation on the Reaction Mechanism: Flame Propagation Studies", 37th Annual North American Thermal Analysis Society (NATAS) Conference, 21-23 September 2009, Lubbock, Texas
6. Farley, C., Pantoya M.L., "Effect of Al Particle Size on the Thermal Analysis of the Al-I₂O₅ Reaction, 37th Annual North American Thermal Analysis Society (NATAS) Conference, 21-23 September 2009, Lubbock, Texas
7. Crane, C., Dunn, J., Pantoya M.L., "Infrared Diagnostics to Examine Energy Transfer to a Target from a Reacting Thermite", 37th Annual North American Thermal Analysis Society (NATAS) Conference, 21-23 September 2009, Lubbock, Texas
8. Stacy, S., Pantoya M.L., Daniel J. Prentice, Eric D. Steffler, and Michael A. Daniels, Underwater Nanometric Aluminum and Polytetrafluoroethylene Combustion, 37th Annual North American Thermal Analysis Society (NATAS) Conference, 21-23 September 2009, Lubbock, Texas
9. The effect of pre-heating on flame propagation in nanocomposite thermites, B. Dikici and ML Pantoya, 47th AIAA Aerospace Sciences Meeting, Paper No. AIAA-2009-1626, 5-8 January 2009, Orlando, FL.
10. "Energy Transport In Nanocomposite Energetic Materials: Mechanisms vs Modes," S. Dean, M. L. Pantoya, A. Gash," 42nd JANNAF Combustion Subcommittee Meeting. Boston, MA: 12-16 May 2008
11. Stacy, S.C.; Pantoya, M.L.; Prentice, D; and Steffler, E. "Hydrodynamics of Deflagrations of Nanometric Aluminum/Teflon Composites Underwater." 42nd JANNAF Combustion Subcommittee Meeting. Boston, MA: 12-16 May 2008
12. "Impact Ignition of Energetic Materials," A. Hunt, A. Purl, E. Hunt, M. L. Pantoya, Materials Research Society, Spring Meeting, San Francisco, CA April, 2008.
13. "Energy Transport In Nanocomposite Energetic Materials: Mechanisms vs Modes," S. Dean, M. L. Pantoya, A. Gash, Central States Section of the Combustion Institute, Tuscaloosa, AL, April 2008.
14. "Nanostructured energetic materials: aerogel thermite composites," A. Gash and M. Pantoya, Division of Polymer Chemistry for the 236th ACS National Meeting, Philadelphia, PA, Aug 17-21, 2007.
15. "Effects of Particle Size on Flame Propagation of Al/Teflon Mixtures," Osborne, D. Watson, K. W., Pantoya, M. L., Proceedings of the 34th North American Thermal Analysis Society Conference (NATAS), p. 129, Aug 5-9 (2006) Bowling Green, Kentucky.
16. "The Effects of Fuel Particle Size on the Thermal Degradation of Al/Teflon Mixtures," Osborne, D. T. and Pantoya, M. L. Proceedings of AIChE-World Congress on Particle Technology 5 April 23-27, 2006, Orlando FL
17. "Heat Flux Measurements of Aluminum Particles in an Acetylene-Oxygen Premixed Flame," White, R.B., Pantoya, M.L., Hirschfeld, D., Gill, W., Erickson, W.W, Proceedings of the 22nd JANNAF Propulsion Systems Hazards Subcommittee JANNAF meeting, Charleston SC (2005).
18. "Combustion Behaviors Resulting from Bimodal Aluminum Size Distributions," K. Moore, M. L. Pantoya, S. F. Son, 41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference, Paper AIAA-2005-3605, Tucson, AZ, June, 2005
19. "Material Characterization of Nano-Structured Al-Ni Intermetallic Composites using Residual Stresses," K. K. Rajamani, I. V. Rivero, M. L. Pantoya, Proceedings of the 2005 Institute of Industrial Engineers (IIE) Annual Conference, May 14-18, Atlanta, Georgia, 2005.

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

19

Peer-Reviewed Conference Proceeding publications (other than abstracts):

1. Dikici B., Pantoya M.L., “The Effect of Pre-heating on Flame Propagation in Nanocomposite Thermite”, ASME Banquet, Poster presentation, 22 April 2010, Lubbock, Texas
2. Dikici B., Pantoya M.L., Shaw B.D. “Analysis of the Influence of Nanometric Aluminum Vaporization on Flame Propagation in Bulk Powder”, Paper Number AIAA-2010-1598, 48th AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition, 4-7 January 2010, Orlando, Florida.
3. Dikici B., Pantoya M.L., “The influence of Aluminum Passivation on the Reaction Mechanism: Flame Propagation Studies”, 37th Annual North American Thermal Analysis Society (NATAS) Conference, 21-23 September 2009, Lubbock, Texas
4. Farley, C., Pantoya M.L., “Effect of Al Particle Size on the Thermal Analysis of the Al- Fe_2O_3 Reaction”, 37th Annual North American Thermal Analysis Society (NATAS) Conference, 21-23 September 2009, Lubbock, Texas
5. Crane, C., Dunn, J., Pantoya M.L., “Infrared Diagnostics to Examine Energy Transfer to a Target from a Reacting Thermite”, 37th Annual North American Thermal Analysis Society (NATAS) Conference, 21-23 September 2009, Lubbock, Texas
6. Stacy, S., Pantoya M.L., Daniel J. Prentice, Eric D. Steffler, and Michael A. Daniels, Underwater Nanometric Aluminum and Polytetrafluoroethylene Combustion, 37th Annual North American Thermal Analysis Society (NATAS) Conference, 21-23 September 2009, Lubbock, Texas
7. Dikici B., Pantoya M.L., “The Effects of Perfluoroalkyl Carboxylic Acid Coating of Al Particles to Flame Propagation”, 2009 ASME International Mechanical Engineering Congress and Exposition, 13-19 November 2009, Lake Buena Vista, Florida
8. “Quantification of Heat Flux from a Reacting Thermite Spray,” E. Nixon, M. L. Pantoya and D.J. Prentice, Proceedings of the 2009 ASME Heat Transfer Conference, July 2009, Paper No. HT 2009-88219.
9. “Quantifying Energy Transfer From a Reacting Thermite to a Target Using Infrared Diagnostics,” C. Crane, M. L. Pantoya, J. Dunn, Proceedings of the 2009 ASME Heat Transfer Conference, July 2009 Paper No. HT2009-88156.
10. Dikici B., Pantoya M.L., “The influence of Aluminum Passivation on the Reaction Mechanism”, 45th AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition, 2-5 August 2009, Denver, Colorado
11. The effect of pre-heating on flame propagation in nanocomposite thermite, B. Dikici and M.L. Pantoya, 47th AIAA Aerospace Sciences Meeting, Paper No. AIAA-2009-1626, 5-8 January 2009, Orlando, FL.

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

11

(d) Manuscripts

1. V.I. Levitas, B. Dikici, M.L. Pantoya, Toward Design of the Prestressed Nano- and Microscale Aluminum Particles Covered by Oxide Shell, Submitted to Combustion and Flame, March 2010.
2. E. M. Hunt and M. L. Pantoya, Synthesis of Antibacterial Metallic NanoFoams, submitted to Nano Research, Oct 2010.
3. C. Farley, T. Turnbull, M. L. Pantoya, E. Hunt, Semi Self Propagating High Temperature Synthesis of Nanostructured Titanium Aluminide Alloys with Varying Porosity, Submitted to Acta Materialia, March 2010.
4. S. Datta, B. Dikici, M.L. Pantoya, S.Ekwaro-Osire, Reaction dynamics and probability study of aluminum-viton-acetone droplets, Accepted to the Journal of Propulsion and Power, April 2010.
5. Keerti S. Kappagantula, Billy Clark, Pantoya, M.L., Analyzing Energy Propagation in Non-Gas Generating Nanocomposite Reactive Materials, submitted to Energy and Fuels, Aug 2010.
6. Crane, C.A., Collins, E.S., Pantoya, M.L. and Weeks, B.L., Nanoscale Investigation of surfaces exposed to a thermite spray, submitted to Journal of Thermal Spray Technology, Aug 2010.
7. E. Nixon, M.L. Pantoya, G. Sivakumar, A. Vijayasai, T. Dallas, Superhydrophobic Coatings for Nanoenergetic Material Combustion, Submitted to Surface Coatings and Technology October 2010.

Number of Manuscripts: 7.00

Patents Submitted

Patents Awarded

Awards

1. F.A.C.E. Award (Faculty Academic Contribution Exhibit),2010
<http://www.facebook.com/video/video.php?v=838340042838>
2. Award Winning Finalist in the Children's Non-Fiction category of the "Best Books 2010" Awards, sponsored by USA Book News
<http://www.usabooknews.com/bestbooks2010.html> 2010
<http://today.ttu.edu/2010/04/elephants-build-future-engineers/>
http://www.youtube.com/watch?v=8NBok0nKPLU&feature=player_embedded
3. Integrated Scholars Award, Texas Tech University, 2010
See You-Tube movie: <http://www.youtube.com/watch?v=iCGftWdk4I8>
4. Ed and Linda Whitacre Faculty Fellow, Texas Tech University, 2008-2011
5. Excellence in Research Award, College of Engineering, TTU(external funding \$ 250-500k), 2008
6. Excellence in Research Award, College of Engineering, TTU(external funding \$ 250-500k), 2007
7. Raymond B. Davis Award, Citizen Hero Award, University Medical Center & City of Lubbock, 2007
8. Texas Tech Outstanding Researcher Award 2006
9. Presidential Early Career Award for Scientists and Engineers (PECASE), 2004
10. Young Investigator Program Award Department of Defense, 2002

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Mr. John Granier	0.50
Mr. Kyle Watson	0.50
Ms. Birce Dikici	0.50
Mr. Randy White	0.50
Mr. Kevin Moore	0.50
Ms. Emily Hunt	0.50
Mr. Daniel Prentice	0.50
Ms. Sanjana Datta	0.50
Mr. Eric Nixon	0.50
Ms. Keerti Kappagantula	0.50
Mr. Cory Farley	0.25
Mr. Shawn Stacy	0.25
Ms. Garima Chauhan	0.25
Mr. Keith Plantier	0.50
Mr. Jonathan Burkhard	0.15
Mr. Steven Dean	0.25
Mr. Dustin Osborne	0.50
Mr. Daniel Prentice	0.50
FTE Equivalent:	7.65
Total Number:	18

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Michelle Pantoya	0.25	No
FTE Equivalent:	0.25	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Travis Turnbull	1.00
Alejandro Bilblao	1.00
Adam Sapp	1.00
Lyle Foutes	1.00
Kevin Moore	1.00
FTE Equivalent:	5.00
Total Number:	5

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 5.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 5.00

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:..... 2.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 5.00

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

<u>NAME</u>
Mr. Keith Plantier
Mr. Kevin Moore
Mr. Randy White
Mr. Daniel Prentice
Mr. Dustin Osborne
Mr. Kyle Watson
Mr. Jonathan Burkhard
Ms. Garima Chauhan
Mr. Shawn Stacy
Mr. Steven Dean
Ms. Sanjana Datta
Mr. Eric Nixon
Total Number:

12

Names of personnel receiving PhDs

<u>NAME</u>
John Granier
Emily Hunt
Birce Dikici
Total Number:

3

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Forward

The Combustion Lab group under the direction of Dr. Michelle Pantoya is deeply grateful for the opportunity to work on Army relevant research that has significantly contributed to the field of energetic materials. Graduates supported under this project have integrated themselves into the energetic materials community within the US. For example, Dr. John Granier is a founder of Energetic Materials Products Inc (EMPI) in Austin, TX. Dr. Emily Hunt is an Associate Professor at West Texas A&M University researching energetic materials for combustion synthesis applications. Daniel Prentice is an energetic materials scientist at Idaho National Laboratory developing thermite materials for ordnance applications. Dustin Osborne works with energetic materials at South West Research Institute (SWRI), Kyle Watson works on demil of energetic materials at PANTEX in Amarillo, TX. Dr. Birce Dikici is an assistant professor at the North Florida University starting her research program in energetic materials and Steven Dean received his MS degree at TTU and is now a PhD student under the direction of Dr. Rich Yetter at PSU.

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 have had the pleasure of working with my program manager, Dr. Ralph Anthenien who listens to all my crazy ideas and remains supportive and encouraging as well as patient. Also, my sincere gratitude toward Dr. David Mann, who helped me get my start in this field 10+ years ago.



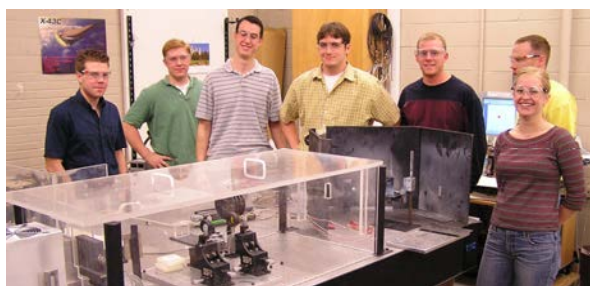
From left to right: Jeremy Reed, William Bender (undergraduate research assistant), Garima Chauhan, Jonathan Burkhard, Michelle Pantoya, Charles Crane, Steven Dean, Shawn Stacy, Birce Dikici 2007



From left to right: Charles Crane, Shawn Stacy, Cory Farley, Steven Dean, Sanjana Datta, Michelle Pantoya, Eric Nixon, Kavya Balupari, Birce Dikici, Billy Clark 2008



Visiting John at EMPI in 2010. John Granier, Shawn Stacy, Michelle Pantoya, Charles Crane and Billy Clark.



In the beginning, 2004: Daniel Prentice, Dustin Osborne, Kevin Moore, John Granier, Randy White, Matt Jackson and Emily Hunt.

Scientific progress and accomplishments

Progress towards understanding the combustion behaviors and performance of nanocomposite energetic materials and their role in weapon systems has been made through understanding the processes controlling ignition, flame propagation, reaction velocities, reaction mechanism and energy transfer as a function of particle size, bulk density and stoichiometry. In the following discussion a summary of the results learned for the 2005-2010 project duration will be highlighted as well as publications detailing each study and students involved. The results are summarized in Items (1) – (5).

- (1) Diagnostic Developments
 - a. Flame Tube Apparatus and Summary of Flame Propagation Studies
 - b. Thermite Spray Apparatus & Heat Flux Sensor
 - c. Laser Flash Analyzer for Thermal Property Measurements
 - d. Differential Thermal Analysis for Equilibrium Kinetic Studies
- (2) Combustion Synthesis Studie
 - a. Nickel Aluminides and Metallic Foams
- (3) Ignition Studies
 - a. Laser Ignition
 - b. Impact Ignition
- (4) Flame Propagation Studies
 - a. Melt Dispersion Mechanism
 - b. Density Effects
- (5) Miscellaneous
 - a. Underwater thermite reactions
 - b. Droplet Combustion with Seeded Al particles
 - c. Debonding, embrittlement and fragmentation
 - d. Energetic materials for energy storage

I. Diagnostic Developments

A. Flame tube apparatus

The unsung hero of our contributions to the investigations of nanocomposite energetic materials was developed in our lab starting in 2004. One of my first graduate students, Bryan Bockmon, was tasked with designing an apparatus that allowed characterization of the reaction front for composites that used nano-Al particles as the fuel.

The *flame tube* has become a bench mark diagnostic for examining flame propagation of nanometric aluminum (nm Al) powders combined with a solid oxidizer. The first study demonstrating this diagnostic was published in 2002 by Bockmon et al. and was used as a tool to characterize the combustion behavior of nm Al combined with molybdenum trioxide (MoO_3). For this reason, the flame tube has also been referred to as the *Bockmon Tube*. Prior to the first reporting of the flame tube, this diagnostic was not useful because micron scale Al particles do not propagate combustion waves well, or at all, in this semi-confined tube. However, with the advent of nanotechnology, nm Al particles are significantly more ignition sensitive such that less energy is required to ignite (and therefore propagate) a reaction.

The flame tube can be described as a long transparent tube (usually 10 cm in length) made out of Acrylic™ or Lexan™ with a constant inside diameter ranging from 3-5 mm and is illustrated in Figure 1 (Appendix). The tube may be machined with sensor ports for monitoring pressure and/or optical light intensity at various axial locations along the tube. These measurements, coupled with high speed imaging of the reaction propagation, provide information about the pressure profile as well as the propagation speed of the luminous reaction front. The propagation speed is typically too fast to allow accurate and simultaneous temperature measurements. Ignition is typically by an electric match or hot wire (thermal ignition) and the tube can be open at one end while the ignition source seals the other end. We examined the sensitivity of the

tube inside diameter on the flame propagation speed and found that for sufficiently small tubes, diameters above roughly 4 mm do not appreciably influence flame propagation speeds. The amount of powder loaded into the tube can vary among experimenters but is typically around 300 mg such that the bulk density of the powdered mixture may range from 3-10% of the theoretical maximum density (TMD). These low percentages of TMD describe the composite as a loose powder (e.g., 3 % solid, 97% void space). It is also interesting to note that the flame tube has been employed by other researchers in inert (argon), vacuum as well as high pressure environments.

Table 1 summarizes flame speeds from much of the literature that incorporate a flame tube measurement for characterizing the combustion of nm Al particles combined with a solid oxidizer. Table 1 highlights general flame speeds of various mixtures; however, many other reported work also utilized the flame tube diagnostic to characterize powder reaction propagation.

Some physical interpretations from Table 1 reveal that reaction propagation falls into mainly 3 categories determined by the behavior of the oxidizer upon nano Al ignition. Studies show that metallic oxidizers that decompose or gasify at temperatures below the adiabatic flame temperature for the reaction result in higher flame propagation rates. In Table 1, this case holds for oxidizers such as CuO, MoO₃, WO₃, Bi₂O₃. Metal oxidizers that decompose or gasify above the adiabatic flame temperature for the reaction likely initiate in the condensed phase, which promote slower propagation speeds. In Table 1, this case holds for Fe₂O₃ and NiO. Finally, a third category may be associated with reducing agents that fall under the halogen family such as fluorine and iodine that typically decompose at temperatures well below the melting temperature of Al and act as aggressive oxidizers partly due to their relatively high electronegativity.

Composition	Al Size (nm)	Active Al Content(%)	Equivalence Ratio	%TMD	Velocity (m/s)	Peak Pressure (MPa)	Ref
Al+MoO ₃	79	81	3.6	9	1025	n/a	[4]
Al+MoO ₃	80	80	1.35	10	989	17.9	[1]
Al+MoO ₃	80	88	1.4	11	950	18.6	[7]
Al+CuO	80	88	1.1	6	802	13.1	[7]
Al+WO ₃	80	88	1.9	9	925	26.9	[7]
	80						
Al+Bi ₂ O ₃	80	88	1.3	17	646	53.4	[7]
Al+Bi ₂ O ₃	80	88	1.3	47	560	39.3	[7]
Al+Fe ₂ O ₃	52	75	1.4	7	617	n/a	[8]
Al+Fe ₂ O ₃	52	75	1.4	7	8	n/a	[8]
Al+Fe ₂ O ₃	50	70	n/a	n/a	25	n/a	[9]
Al+NiO	50	75	2.5	7	194	1.68	[10]
Al+Teflon	50	75	1.39	9	837	14.37	[11]
Al+I ₂ O ₅	80	80	1.25	7	1305	28	[12]

Table 1. Flame speeds from flame tube measurements characterizing the combustion of nm Al particles combined with a solid oxidizer. The references reported in this table correspond with those documented in [1].

This summary comprises results from the following publications listed above but bulleted below:

- [1] Shaw, B., Pantoya, M.L., Dikici, B., “Detonation models for fast propagation speeds of nano-composite thermite reactions in bulk powder media,” Pending submission to Combustion Theory and Modeling.
- “Combustion Wave Speeds of Nanocomposite Al/Fe₂O₃: The Effects of Fe₂O₃ Particle Synthesis Technique,” K. B. Plantier, M. L. Pantoya and A. E. Gash, *Combustion and Flame* 140(4), 299-309 (2005) [DOI: 10.1016/j.combustflame.2004.10.009].
 - “Combustion Velocities and Propagation Mechanisms of Meta-stable Intermolecular Composites,” B. S. Bockmon, M. L. Pantoya, S. F. Son, B. W. Asay, J. T. Mang, *Journal of Applied Physics* 98(6), 064903 (2005) [DOI: 10.1063/1.2058175].
 - “Combustion Behaviors of Highly Energetic Thermites: Nano versus Micron Composites,” M. L. Pantoya and J. J. Granier, *Propellants, Explosives, Pyrotechnics* 30(1), 53-62 (2005) [DOI: 10.1002/200400085].
 - “Combustion Effects of Environmentally Altered Molybdenum Trioxide Nanocomposites,” K. Moore and M. L. Pantoya, *Propellants Explosives Pyrotechnics* 31(3), 182-187 (2006).
 - “Combustion Behaviors Resulting from Bimodal Aluminum Size Distributions in Thermites,” K. Moore, M. L. Pantoya, and S. F. Son, *Journal of Propulsion and Power* 23(1), 181-185 (2007). [DOI: 10.2514/1.20754]
 - “Combustion Wave Speeds of Sol-gel Synthesized Tungsten Trioxide and Nano-Aluminum: The Effect of Impurities on Flame Propagation,” D. Prentice, M. L. Pantoya, and A. E. Gash, *Energy & Fuels* 20(6), 2370-2376 (2006). [DOI:10.1021/ef060210i].
 - “Mechanochemical Mechanism for Fast Reaction of Metastable Intermolecular Composites Based on Dispersion of Liquid Metal,” V. I. Levitas, B. W. Asay, S. F. Son and M. L. Pantoya, *Journal of Applied Physics* 101(8), 083524 (2007). [DOI: 10.1063/1.2720182]
 - “Melt-Dispersion versus Diffusive Oxidation Mechanism for Aluminum Nanoparticles: Critical Experiments and Controlling Parameters,” V. I. Levitas, Pantoya, M. L., B. Dikici, *Applied Physics Letters* 92(1), 0011921 (2008). [DOI:10.1063/1.2824392]
 - “Fast reactions with nano and micron aluminum: a study on oxidation versus fluorination,” K.W. Watson, M. L. Pantoya, V. I. Levitas, *Combustion and Flame* 155(4); 619-634 (2008).
 - “The Influence of Aluminum Passivation on the Reaction Mechanism: Flame Propagation Studies”, B. Dikici, M.L. Pantoya, Levitas, V., R.J. Jouet, *Energy & Fuels* 23, p4231-4235 (2009). DOI:10.1021/ef801116x.
 - S.W. Dean, M.L. Pantoya, A.E. Gash, S.C. Stacy, L. Hope-Weeks, “Enhanced Convective Heat Transfer from Non-gas Generating Nanoscale Thermite Reactions,” *Journal of Heat Transfer* 132(11), 2010; DOI: 10.1115/1.4001933.
 - Dikici, M.L. Pantoya, V. Levitas, The Effect of Pre-heating on Flame Propagation Behavior in Nanocomposite Thermites, *Combustion and Flame*, v157(8); 1581-1585 (2010).

B. Thermite Spray Apparatus and Heat Flux Sensor

The motivation for developing a thermite spray apparatus was for the need to understand how jets of thermite spray interact with materials. When a thermite spray is impinging on a granular propellant bed (i.e., for igniter applications) or on solid metal substrates (i.e., for cutting applications); these are two examples of applications for which the thermite spray may be subjected.

This pursuit began with an investigation on how a hydrocarbon spray’s energy transfer may be enhanced if seeded with Al particles. The result was an over 80% increase in energy transfer for jets that were seeded with reactive Al particles compared with jets not seeded or seeded with inert particles, see Figure 2 (Appendix).

That study led to the development of the thermite spray gun that showed once ignited the high gas generating thermite spray projects out of the jet nozzle at high velocities (i.e., on the order of 50 m/s) and the stream continues to react at distances up to 5-nozzle diameters downstream of the nozzle exit. This was shown with heat flux measurements which revealed that the highest temperatures and heat flux are not at the nozzle exit but can vary downstream of the nozzle exit depending on the gas generating properties of the reactants.

There is a distinct variation in burning behavior with fuel particle size. The nano-Al formulation produced a dispersed stream with very little penetration of the Si target. In contrast, the micron-Al formulation produced a focused stream with complete penetration of the Si target, see Figure 3 (Appendix).

The heat flux sensor was developed as a means to characterize and quantify the energy release of a thermite reaction impinging on a surface. Off-the-shelf sensors simply do not work because (1) they are destroyed in the highly corrosive environments of the reaction; and/or (2) they do not provide the time response to enable highly transient fluctuations in heat flux to be quantified. Our lab developed an initial proto-type sensor that has been transferred to APG for continued use and experimentation on their super igniter program.

Work will hopefully continue using this thermite spray nozzle and heat flux sensor to understand how the energy from the spray may be directed toward the two applications highlighted above. The following publications highlight this work in detail.

- A Diagnostic for Quantifying Heat Flux from a Thermite Spray, EP Nixon, ML Pantoya, DJ Prentice, ED Steffler, MA Daniels, and SP D'Arche, *Measurement Science and Technology*, 21: 025202; 2010.
- "The Effect Of Aluminum On The Heat Flux From A Simulated Rocket Propellant Flame," R. B. White, S. W. Dean, M. L. Pantoya, D. A. Hirschfeld, W. Gill and W. W. Erikson, *Journal of Propulsion and Power* 23(6), 1255-1262 (2007). [DOI: 10.2514/1.28161].
- "Characterization of a gas burner to simulate a propellant flame and evaluate aluminum particle combustion," M. Jackson, M. L. Pantoya and W. Gill, *Combustion and Flame* 153(1-2), 58-70 (2008).

C. Laser Flash Analyzer

The LFA is a new diagnostic purchased for the need to understand energy propagation through many thermite or reactive material composites, see Figure 4 (Appendix). Many reactions are controlled by thermal diffusion yet the thermal properties of mixtures are a strong function of reactant morphologies, bulk density, particle size and even temperature. These properties are often determined by weighted averages of bulk material properties. These approximations are used in models to understand ignition and energy propagation behaviors. To the author's knowledge, there was previously no systematic experimental determination of just how much the basic thermal properties are influenced by changes in parameters such as particle size. The LFA measures these properties for bulk powders, consolidated pellets or even liquid mediums and is the first diagnostic in the energetic material specialty to quantify thermal properties of reactive materials. Results are just beginning to be realized and will be reported in years to come.

D. Differential thermal analysis (DTA) for equilibrium kinetic studies

One paradox in working with nanocomposite materials is how heating rate controls the reaction mechanism. Slow, controlled heating rates of up to 20 degrees per minute correspond with an equilibrium analysis of the material because the reaction is always controlled from thermal run away. For example, if you turn off the DTA, the reaction will stop too. These equilibrium studies offer much insight into the first and primary steps in faster reactions but can also imply misleading information if the researcher assumes that equilibrium reaction dynamics directly translate to non-equilibrium reaction dynamics.

The first studies we pursued using our DTA revealed that nano-Al particles exhibit reduced melting temperature in accordance with the Gibbs Thompson Equation. While this had been shown for materials such as tin and gold, our study was one of the first to report this for nano-Al particles.

Additional studies revealed that nano-Al initiates reaction at temperatures about equal to its melting temperature (roughly 660 C) while micron scale counterparts do not initiate reaction until much higher temperatures, see Figure 5 (Appendix). This was the first understanding for why non-equilibrium studies showed three orders of magnitude heightened ignition sensitivity associated with nano-particles as opposed to micron particles.

Following these oxidation related studies, we investigated the Al – fluorine reaction by studying Al – Teflon. The interesting finding here was that the halogen, F, is so highly reactive, that it actually reacts with the alumina shell surrounding the Al particles. The extraction of F from Teflon and immediate bonding of F to

alumina was discovered to be the first step in the Al-Teflon reaction, see Figure 6 (Appendix). Another interesting revelation was that the attraction between F and alumina could be controlled by the surface area of the alumina (or Al particle size). This discovery led to an understanding that the decomposition temperature of Teflon (and other fluoropolymers) could be controlled by the Al particle size. As alumina surface area is increased, Teflon decomposition temperature could be reduced by up to 60 degrees.

Additional work with our DTA has enabled us to quantify gas species evolved from reactions. This complement to our DTA is relatively new with little published on the impactful results that the increased characterization will allow us to resolve. On-going work is planned to utilize the gas chromatography capabilities of this diagnostic.

The following publications highlight the work using the DTA.

- “Dependence of size and size distribution on reactivity of aluminum nanoparticles in reactions with oxygen and MoO_3 ,” J. Sun, M. L. Pantoya, and S. L. Simon, *Thermochimica Acta* 444(2), 117-127 (2006).
- “The Effect of Slow Heating Rates on the Reaction Mechanisms of Nano and Micron Composite Thermite Reactions,” J. J. Granier and M. L. Pantoya, *J. of Thermal Analysis and Calorimetry* 85(1), 37-43 (2006).
- “Effect of Aluminum Particle Size on the Thermal Degradation of Al/Teflon Mixtures,” D. T. Osborne and M. L. Pantoya, *Combustion Science and Technology* 179(8), 1467-1480 (2007).
- “The influence of alumina passivation on nano-Al/Teflon reactions,” S.W. Dean and M.L. Pantoya, *Thermochimica Acta* 493(1-2), p 109-110 (2009).
- “Effect of the alumina shell on the melting temperature depression for nano-aluminum particles,” V.I. Levitas, M.L. Pantoya, G. Chauhan, and I. Rivero, *Journal of Physical Chemistry C*, 113(2), p 14088-14096, 2009.
- C. Farley and M.L. Pantoya, Reaction Kinetics of Nanometric Aluminum and Iodine Pentoxide, *Journal of Thermal Analysis and Calorimetry* 102(2), 609-613 (2010) DOI: 10.1007/s10973-010-0915-5.

II. Combustion Synthesis Studies

Thermite reactions can be used not only for generating energy, but also for creating new alloys. The potential to examine combustion synthesis using nanoparticles to generate metal-metal alloys for Army applications prompted us to explore some of these reactions in depth.

A. Nickel aluminides and metallic foams

Our lab was the first to characterize ignition and reaction propagation using nanoparticles of nickel and aluminum. The reaction dynamics were compared to the traditional micron scale particles and found to exhibit reduced ignition delay times and increased flame propagation rates governed mainly by diffusive energy transfer (i.e., very little gas was generated during these reactions such that convection was minimal).

These characterizations continued past reactive behavior and also explored the product microstructure of the nickel aluminide. Further studies revealed that nickel aluminide synthesized via combustion synthesis produced a more corrosive resistant alloy with a more pure (fewer impurities) microstructure. Much of the improved physical properties of the NiAl alloy were attributed to the greater concentration of alumina associated with nanoparticles that are an inherent part of the Al particles.

We added more energetic reactants to the Ni and Al reactant matrix and discovered that higher heating rates during the synthesis process results in more homogeneous microstructure of the NiAl product. This work showed that the heating rate during the self propagating high temperature synthesis has a direct impact on the formation of the product microstructure.

We also showed that by adding small amounts of nano-particle reactants that generate gas upon reaction, we could control the porosity of the NiAl alloy. More gas generators in the reactant matrix lead to greater porosity in the product microstructure such that metallic foams could be synthesized. The real impact in this work was generating nano-porous metallic foams with surface areas higher than any other porous metallic materials that we could find. There is tremendous potential for using these porous metallic foams as catalysis

beds in many combustion systems, as scaffolds in biomedical applications or as platforms for the destruction of bacteria. These avenues are further being explored by our research group. The following articles highlight these findings.

- “The Role of the Al_2O_3 Passivation Shell Surrounding Nano-Aluminum Particles in the Combustion Synthesis of NiAl ,” J. J. Granier, K. B. Plantier and M. L. Pantoya, *Journal of Materials Science* 39(21), 6421-6431 (2004).
- “Nickel Aluminum Superalloys Created by the Self-propagating High-temperature Synthesis (SHS) of Nano-particle Reactants,” E. M. Hunt, J. J. Granier, K. B. Plantier and M. L. Pantoya, *Journal of Materials Research* 19(10), 3028-3036 (2004).
- “Nano-scale Reactants in the Self-Propagating High-Temperature Synthesis of Nickel Aluminide,” E. Hunt, K. Plantier, M. Pantoya, *Acta Materialia* 52(11), 3183-3191 (2004).
- “Combustion Synthesis of Metallic Foams from Nanocomposite Reactants,” E. M. Hunt, M. L. Pantoya and R. J. Jouet, *Intermetallics* 14 (6), 620-629 (2006).

III. Ignition Studies

A. Laser initiation: Experimental and Numerical

Thermal initiation of energetic materials is a fundamental characterization of how ignition dynamics associated with nanoparticles are uniquely different than micron-scale particles. The ignition studies pursued here were the first to quantify the ignition delay time of a nanoparticle composite which is two to three orders of magnitude faster than their micron scale counterpart, see Figure 7 (Appendix). This work revealed that under controlled laser energy input, the ignition delay observed in micron-composites was so long that the thermite experienced pre-heating prior to ignition. That pre-heating led to flame propagation that was faster in micron scale composites as opposed to nanocomposites. These studies inadvertently introduced another parameter that very much influences flame propagation behavior: initial reactant temperature. Further study on this topic ensued and will be discussed later.

The flame propagation observed in the consolidated pellets exposed to the laser ignition source appeared parabolic in nature. This analysis was pursued further using numerical models to show that hot spot formation can occur when the initiation source has a non-uniform distribution energy. Under these conditions, the hot spots grow where energy peaks and reactions propagate from the point source, or quench of the source is extinguished.

Our research also examined the non-equilibrium activation energy of a reactant mixture. While activation energy may technically be the same for all materials assuming a given reaction, the reality is that the “apparent” activation is a strong function of particle size and heating rate. We introduced an iso-conversion method for quantifying apparent activation energy by controlling the laser energy input into a thermite. We showed that nanocomposites produce activation energies two orders of magnitude smaller than their micronscale counterparts. This enhanced ignition results for the higher surface energy manifested on the surface of the particles.

- “Non-Uniform Laser Ignition in Energetic Materials,” J. Granier, T. Mullen and M. L. Pantoya, *Combustion Science and Technology* 175(11), 1929-1951, (2003).
- “Laser Ignition of Nanocomposite Thermites,” J. Granier and M. Pantoya, *Combustion and Flame* 138(4), 373-383 (2004) [DOI: 10.1016/j.combustflame.2004.05.006].
- “Ignition Dynamics and Activation Energies of Metallic Thermites: From Nano- to Micron-scale Particulate Composites,” E. M. Hunt and M. L. Pantoya, *Journal of Applied Physics* 98(3), 034909 (2005). [DOI:10.1016/j.combustflame.2004.10.009]

B. Impact initiation

The interesting difference between thermal and mechanical (i.e., impact) initiation led to further studies on ignition of nanocomposite materials. We developed an in house drop weight impact tester to quantify ignition energy upon impact of the samples. We found some interesting results: (1) impact initiation results in only slight differences in ignition energy as a function of particle size; (2) the ignition energy for impact and thermal ignition of micron composites is on the same order of magnitude; and, (3) the more dense the reactant matrix, the less energy required for ignition. These findings led to the hypothesis that the reaction mechanism associated with nanoparticles is not only a function of the initiation source but also a function of particle size. This conclusion led to more rigorous development of new theories to understand unique behaviors associated with nanoparticles.

- E. M. Hunt and M. L. Pantoya, Impact Sensitivity of Intermetallic Nanocomposites: A Study on Compositional and Bulk Density, *Intermetallics*, v18(8); 1612-1616 (2010).
- “Impact Ignition of nano and micron composite energetic materials,” A. Hunt, A. Purl, E.M. Hunt and M.L. Pantoya, *International Journal of Impact Engineering*, v36 n 6, p842-846 (2009).

IV. Flame Propagation Studies

Much of our flame propagation studies have been highlighted in the flame tube diagnostic section above but this diagnostic was also used to examine macroscopic implications of a new reaction mechanism associated with nanoparticles. The melt dispersion mechanism was introduced as a way of explaining the enhanced reactivity associated with nanoparticles by theorizing that diffusion reactions could be accelerated if the molten core of an Al particle was dispersed. The idea can be described as a bursting of an Al particle that results in droplets of fuel dispersed and oxidized at an accelerated rate.

A. Melt Dispersion Mechanism

This theory predicts certain behaviors on a macroscopic scale that could be tested by strategically designed experiments using the flame tube apparatus. In particular, we showed that a relationship exists between the flame speed and the ratio of shell thickness to Al particle diameter, see Figure 8 (Appendix). Diffusion theory predicts the flame speed increases with the inverse square of the particle diameter. This diffusion based correlation could not be observed in numerous experiments with a variety of nano-Al particles. However, when this data was re-plotted as a function of ratio of alumina shell thickness to Al particle diameter, the correlation between theory and experiment was perfect.

We showed that when the alumina shell is removed from the Al particle, the reactivity of the Al particles is actually inhibited. One premise of the melt dispersion theory is that the shell maintains a pristine condition free of imperfections (i.e., cracks, fractures). When we ball-milled the Al particles, the grinding process introduces cracks and imperfections in the shell, disabling the melt dispersion mechanism. This was shown by reduced flame speeds associated with ‘damaged’ Al particles.

Melt dispersion applies to Al oxidation but further results showed that the mechanism is also applicable to reactions between Al and fluorine (fluorination reactions) and further with Al and iodine (iodination reactions).

Pre-heating Al particles then cooling the particles at a specified rate can relax internal stresses with the particles. In this way, the more of the core can become molten prior to the bursting of the particle. In this way, a more complete combustion reaction would suggest higher flame speeds. This experiment was performed by using a coil heater to heat the samples prior to ignition. Cooling chambers were also used to speed up the rate at which cooling occurred. Particles that cooled at the highest rate were predicted to have greater stress relaxation. This was shown in corresponding experiments to be true.

- “Melt Dispersion Mechanism for Fast Reaction of Nanothermites,” Levitas, V. I., Asay, B. W., Son, S. F., and Pantoya, M. L., *Applied Physics Letters* 89(7), 071909 (2006). [DOI: 10.1063/1.2335362] (Reprod. in *Virtual J. Nanoscale Sci. & Techn.*, 2006, Aug. 28)

- “Mechanochemical Mechanism for Fast Reaction of Metastable Intermolecular Composites Based on Dispersion of Liquid Metal,” V. I. Levitas, B. W. Asay, S. F. Son and M. L. Pantoya, *Journal of Applied Physics* 101(8), 083524 (2007). [DOI: 10.1063/1.2720182]
- “Melt-Dispersion versus Diffusive Oxidation Mechanism for Aluminum Nanoparticles: Critical Experiments and Controlling Parameters,” V. I. Levitas, Pantoya, M. L., B. Dikici, *Applied Physics Letters* 92(1), 0011921 (2008). [DOI:10.1063/1.2824392]
- “Melt-dispersion mechanism for fast reaction of aluminum particles: Extension for micron scale particles and fluorination,” Levitas, V. I., Pantoya, M. L.; Watson, K. W. *Applied Physics Letters*, v 92, n 20, 2008, p 201917
- V.I. Levitas and M.L. Pantoya, “Mechanochemical Mechanism for Fast Reaction of Metastable Intermolecular Composites Based on Dispersion of Liquid Metal, *International Journal of Energetic Materials and Chemical Propulsion* 7(1), 2008.
- “Fast reactions with nano and micron aluminum: a study on oxidation versus fluorination,” K.W. Watson, M. L. Pantoya, V. I. Levitas, *Combustion and Flame* 155(4); 619-634 (2008).
- “The Influence of Aluminum Passivation on the Reaction Mechanism: Flame Propagation Studies”, B. Dikici, M.L. Pantoya, Levitas, V., R.J. Jouet, *Energy & Fuels* 23, p4231-4235 (2009).
- “Effect of the alumina shell on the melting temperature depression for nano-aluminum particles,” V.I. Levitas, M.L. Pantoya, G. Chauhan, and I. Rivero, *Journal of Physical Chemistry C*, 113(2), p 14088-14096, 2009.
- B. Dikici, M.L. Pantoya, V. Levitas, The Effect of Pre-heating on Flame Propagation Behavior in Nanocomposite Thermites, *Combustion and Flame*, v157(8); 1581-1585 (2010).

B. Density Effects

One parameter effecting how energy transports through particle media is the bulk density. We showed a completely paradoxical behavior between nano and micro scale composites (see Figure 9, Appendix). As the density increased the micron-scale composites exhibit an increase in flame speed while the nanocomposite exhibits a decrease in flame speed. One suggestion for this paradox was the in-activation of the melt dispersion mechanism as the nanocomposite bulk density increased. More pressure and force are required to consolidate the nanoparticles media, implying more grinding between particles and deformations within the alumina shell. These imperfections would lead to inactivation of the dispersion mechanism and may be a consequence of the reduced flame speeds. Another contributing factor may be hidden within the thermal properties of the mixture. Currently LFA work reveals that the micron particles show up to 30% improved thermal diffusivity over their nanoscale counterparts, owing mainly to the increased alumina content of the nanocomposite. As density increases, thermal properties of the mixture become more important because convection plays a smaller role in energy propagation. The inherent changes in thermal properties may be one explanation for the paradox.

- “The effect of bulk density on the reaction dynamics in nano and micron particulate thermites,” M. L. Pantoya, V. I. Levitas, J. J. Granier, J. B. Henderson, *Journal of Propulsion and Power* 25(2); March-April (2009).

V. Miscellaneous

The unique combustion behaviors observed in the above experiments led to new ways of thinking about how nanocomposites may behave in diverse environments. The following experiments briefly describe experiments that have made an impact on niche areas.

A. Underwater thermite reactions

Thermite reactions do not typically propagate underwater. The problem is that the water extracts more energy from the reaction than needed to sustain self propagation. The result is that the reaction quenches. However, nanoparticles require less energy to ignite, and therefore self propagate. This is especially true if part of the reactant matrix contains hydrophobic material that would prevent water from penetrating into the

mixture. For these original experiments, we employed a simple Al-Teflon mixture and designed and constructed an aquarium chamber to examine the reactivity of the nanocomposites underwater. The result was add new perspectives on nanoparticles burning, namely: micron Al particles quench when submerged with a hydrophobic oxidizer while nano-Al particles react to completion, see Figure 10, Appendix. The interesting observations in this work included the hydrodynamics associated with bubble formation. As the density of the pellet increased, the reaction transitioned from a single gas bubble elevated over time to a jet stream of many smaller bubbles. The energy displaced by the reaction was also computed.

Follow on work used an Al-Fe₂O₃ composite that was coated with a hydrophobic coating. The nano-layer coating prevented water permeation into the matrix and enabled the composite to reaction to completion several months after being immersed. The other interesting finding from this work was the order of magnitude increase in displaced energy from the reaction. This suggests that thermite can now be used for underwater applications where they had not been applicable in the past.

- “Aluminum Fueled Nanocomposites for Underwater Reaction Propagation,” S.C. Stacy, M.L. Pantoya, D.J. Prentice, M.A. Daniels, E.D Steffler, *Advanced Materials and Processes* 167(10) p 33-35, Aug 2009.
- E. Nixon, M.L. Pantoya, G. Sivakumar, A. Vijayasai, T. Dallas, Superhydrophobic Coatings for Nanoenergetic Material Combustion, Submitted to *Surface Coatings and Technology* October 2010.

B. Droplet combustion with seeded Al particles

Droplet combustion studies were pursued to examine the influence of nano-Al particles on the combustion behaviors of acetone and Viton dissolved in acetone. Results showed a multistage process that included droplet evaporation, followed by combustion of the liquid hydrocarbon, followed by disruptive burning associated with reaction among discrete Al particles within the liquid mixture and subsequent reaction of agglomerated Al particles. The disruptive burning was not present with micron particles that were concluded to be too large in size to participate in this phase of reaction. Also, the final stage associated with Al burning was more significant for micron scale particles.

- S. Datta, B. Dikici, M.L. Pantoya, S.Ekwaro-Osire, Reaction dynamics and probability study of aluminum-viton-acetone droplets, Accepted to the *Journal of Propulsion and Power*, April 2010.

C. Debonding, embrittlement and fragmentation

A group at APG expressed interest in using thermite reactions to embrittle steel. The idea was to alter the steel's properties, subtly, to allow a fracture or destruction of a system without the attention of an explosion. The reaction would generate enough heat to alter the properties of the steel, embrittling the steel. The initial tests employed a boron formulation as boron was the key to the embrittlement reaction between B and carbon in the steel. The problem was that the reaction simply did not achieve temperatures high enough to facilitate the embrittlement reaction. These initial tests did employ a unique diagnostic that enabled high speed IR images of the heated surface. This was the first study to show how energy transfers from a thermite reaction into a steel target on a multi-scale and multi-dimensional level, see Figure 11 (Appendix). While this publication reveals temperatures too low to cause embrittlement, further investigation revealed that the key to forcing an embrittling reaction was in increasing the temperature of the reaction front. The ingredient needed to accomplish this was tantalum (Ta). This unique fuel burns extremely hot and can raise the amount of energy transferred into the steel by an order of magnitude. While we achieved embrittlement using a 30-40% Ta addition to a B and Fe₂O₃ mixture, these combinations were not reported in the literature (for security purposes).

- Charles A. Crane, Michelle L. Pantoya, Jerry Dunn, “Evaluating Energy Transfer from Energetic Materials to Steel Substrates,” *International Journal of Thermal Science* 49(10) 1877-1885, 2010.

D. Energetic materials for energy storage applications

One application in which energetic materials has not weaseled its way into is energy storage; at least, until now. Metal composites inherently have high energy capacitance properties. This property could be exploited in an ‘energetic battery’ application. The idea is to use the high capacitance of the metal composite to store energy from a source (such as thermal energy storage from a solar cell). The composite has such a high thermal inertia that it can maintain a high temperature for an extended duration, storing energy received in the form of thermal energy. When needed, the energetic reaction could be triggered to produce energy that could then be used (see Figure 12, Appendix).

The right mixture for this application would need to be very slow burning with little to no gas generation. The formulations speculated to be ideal are incendiary or time delay formulations. We investigated a candidate formation for basic characterization of ignition and reaction propagation behavior. This mixture was manganese (Mn) combined with MnO_2 . This proved to be a very interesting study because it revealed that the passivation shell coating the Mn particles (comprised of Mn_3O_4) actually participates in the reaction. Unlike Al where alumina is considered a barrier to the reaction and ‘dead weight’, the Mn_3O_4 facilitates the many Mn_xO_y phase transitions that result in a final most stable manganese oxide phase.

- M. Pantoya and E. Hunt, Nanochargers: Energetic Materials for Energy Storage, *Applied Physics Letters* 95; 253101 (2009). (Reprod. in *Virtual J. Nanoscale Sci. & Techn.*, 21(2) 2010, Jan. 11.
- Keerti S. Kappagantula, Billy Clark, Pantoya, M.L., Analyzing Energy Propagation in Non-Gas Generating Nanocomposite Reactive Materials, submitted to *Energy and Fuels*, Aug 2010.

While we have published many papers and graduated many students (many of whom have gone on to work in the energetic materials field) our most impactful contribution has been to the development and integration of nanoparticles into the forefront of ordnance applications. We are grateful to have the opportunity to focus our research in this interesting and rewarding direction.

Technology Transfer

Throughout this project, my students and I have visited with Aberdeen Proving Ground yearly and worked with them on issues relevant to their work. Our collaborations have also extended beyond the military to national laboratories, other universities and industry.

Within APG we have worked with Drs. Richard Beyer, Berrie Homan, Stephen Howard, Brad Forch and Jim Hirvonen. In particular, we transitioned our heat flux sensor diagnostics to Stephen Howard’s super igniter program to improve the characterization of the many flame sprays generated by thermite formulations. We are currently improving this diagnostic by increasing the response time to enable integration into Berrie Homan’s enhanced blast work. We collaborated with Dr. Jason Jouet from Indian Head Naval Surface Warfare Center to examine combustion performance of their acid coated nano-Al particles. That study resulted in a paper that showed the gas generating shell enabled the creating of metallic foams of Ni-Al.

Within industry, we are working closely with Dr. Kurt Schroder and many others from NovaCentrix in Austin, Texas as well as Dr. John Granier and Dr. Dennis Wilson from EMPI to characterize the detonation energy of their tailored formulations.

Throughout this project we have collaborated with scientists from LANL, LLNL, SNL and INL. At LANL we worked with Steven Son on our initial flame tube experiments. At LLNL we consistently worked with Alex Gash to characterize his sol gel synthesized formulations. At SNL we worked with Dr. Walt Gil in the Fire Science and Technology division to examine the heat flux increase in hydrocarbon jet flames seeded with Al particles. At INL we continue to work with their thermite experts on developing and understanding the

parameters that influence the thermite spray gun apparatus. Their purposes lie mainly in torch and cutting technologies. Our similar interests relate to the ejection of the spray onto a propellant granular bed.

Appendix

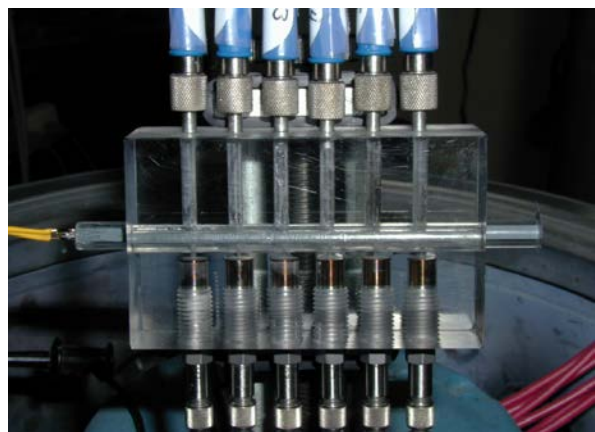
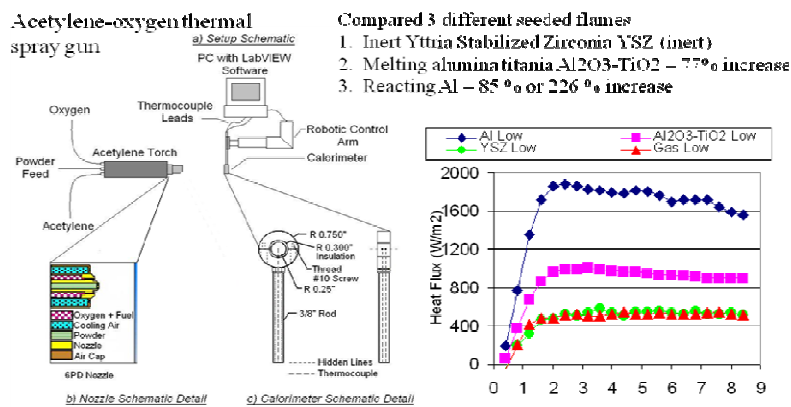


Figure 1. The “Bockmon Tube” a bench mark in characterizing nanocomposite energetic material propagation. Tube is constructed from Lexane with sensor taps for pressure and optical fibers. Inside tube is 10 cm long and roughly 33 mm inside diameter.



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Figure 2. An acetylene-oxygen thermal spray gun seeded with various particles showing that the heat flux is increased by 80% when Al is used as the seeding agent.

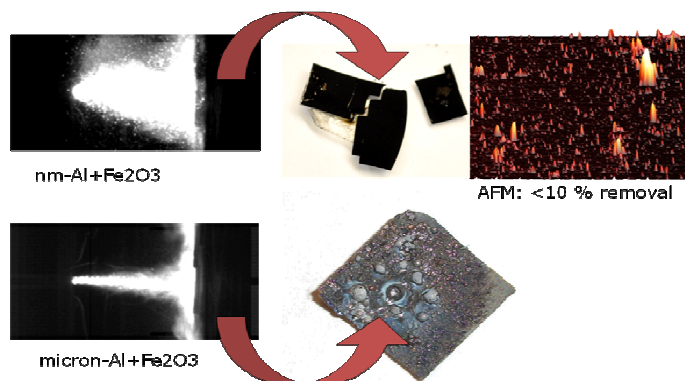


Figure 3. Thermite spray apparatus showing that the nanocomposite formulation produces a dispersed spray and achieves little penetration of Si target while micron composite achieves a focused spray with complete penetration of the target.

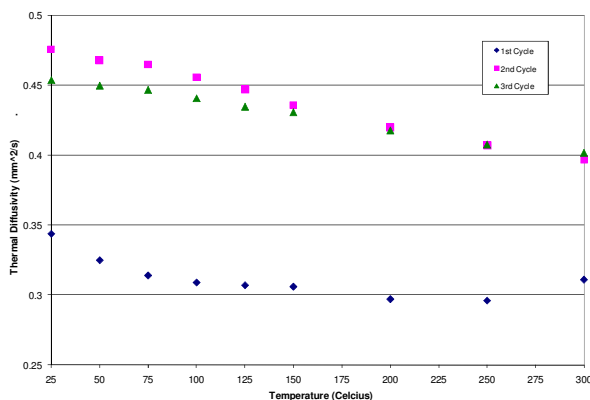
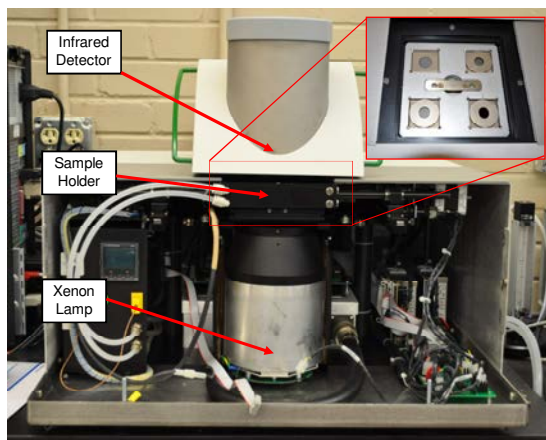


Figure 4. A. Photo of the Laser Flash Analyzer for thermal diffusivity measurements. Note the inset shows the sample carrier holding 4 pellets (3 Al-Fe₂O₃ pellets plus the reference material); B. Thermal diffusivity as a function of temperature for nano-Al+Fe₂O₃ pellets pressed to 40%TMD (this work has not yet been published).

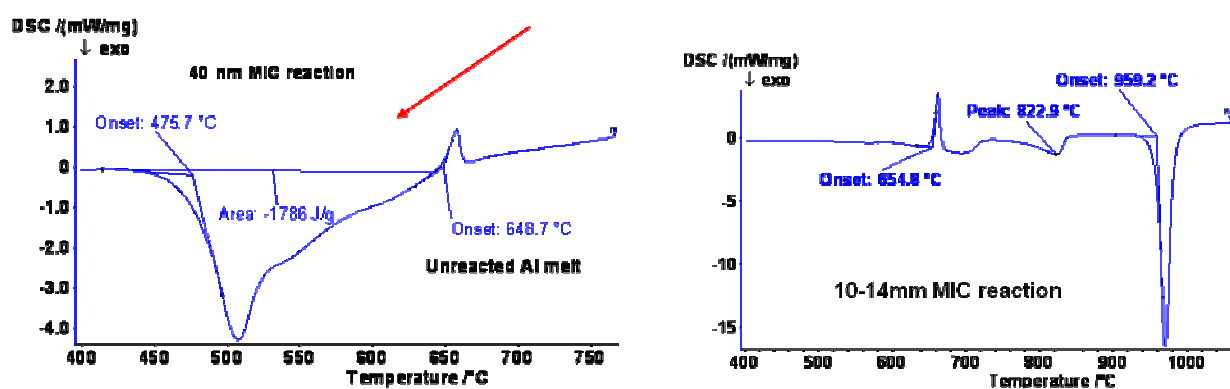


Figure 5. Heat flow curves for Al+MoO₃ composites in DSC under thermal equilibrium conditions. Note nano mixture on the left and micron mixture is on the right. Arrow indicate strong exotherm prior to Al melting temperature.

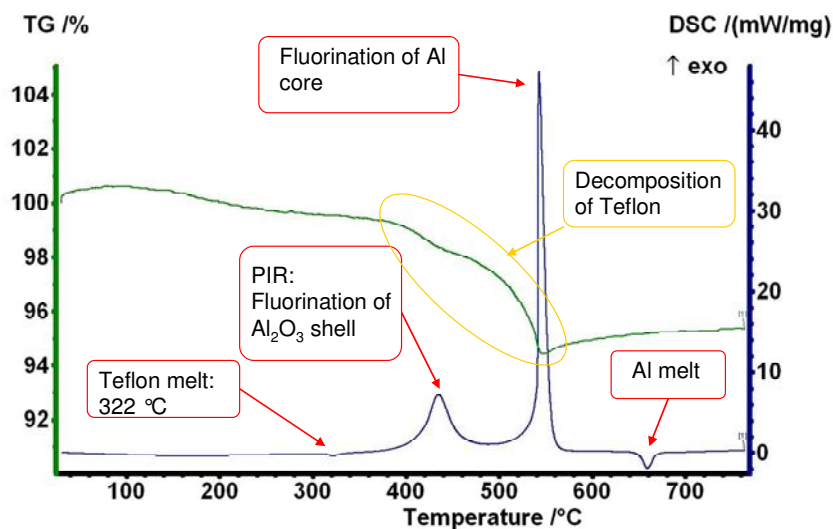


Figure 6. Heat flow and mass loss curves for the nano-Al and Teflon reaction in a DSC-TGA (10 degrees per minute heating rate). The pre-ignition reaction (PIR) is only significant in nano-Al mixtures and corresponds with F extraction from Teflon and bonding with the alumina shell.

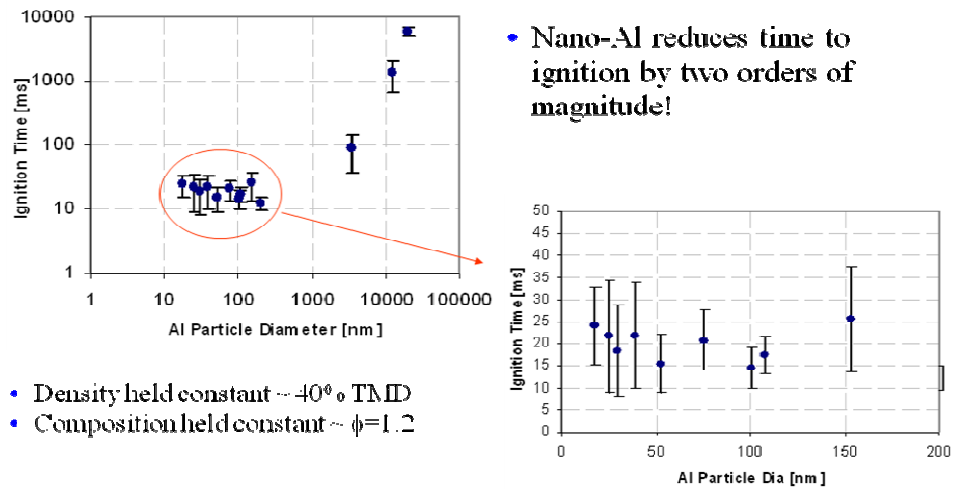


Figure 7. Laser ignition of Al+MoO₃ samples showing that nanoparticles reduce ignition time by two-three orders of magnitude.

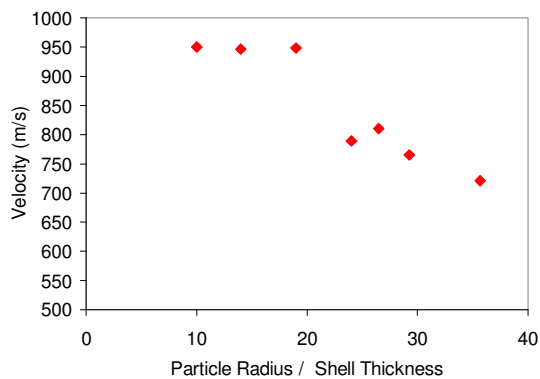


Figure 8. Relationship between velocities measured using the flame tube for Al+MoO₃ mixtures as a function of the Al particle radius to alumina shell thickness ratio.

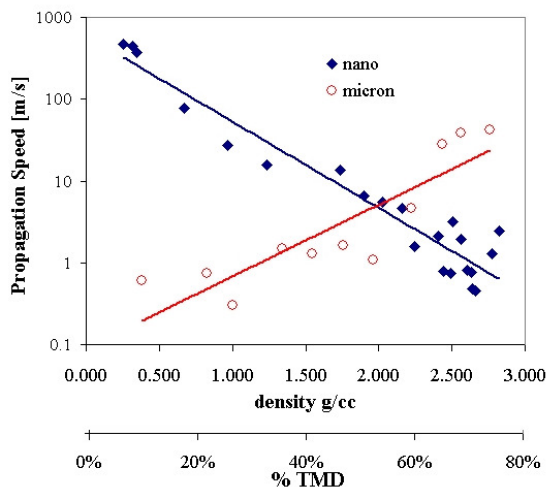


Figure 9. Data for Al+MoO₃ reaction propagation in various bulk density samples for micron (red circle data) to nano (blue diamond data) composites.

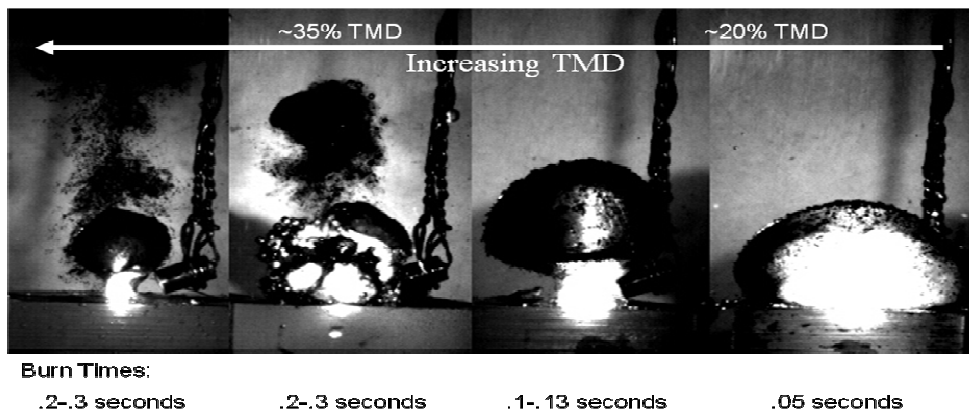


Figure 10. Underwater thermite reactions using nano-Al and hydrophobic Teflon. Images show variation in hydrodynamics with pellet bulk density.

IR images



Figure 11. IR still frame image showing heat transfer from thermite powder into a steel target V-notch for embrittlement applications.

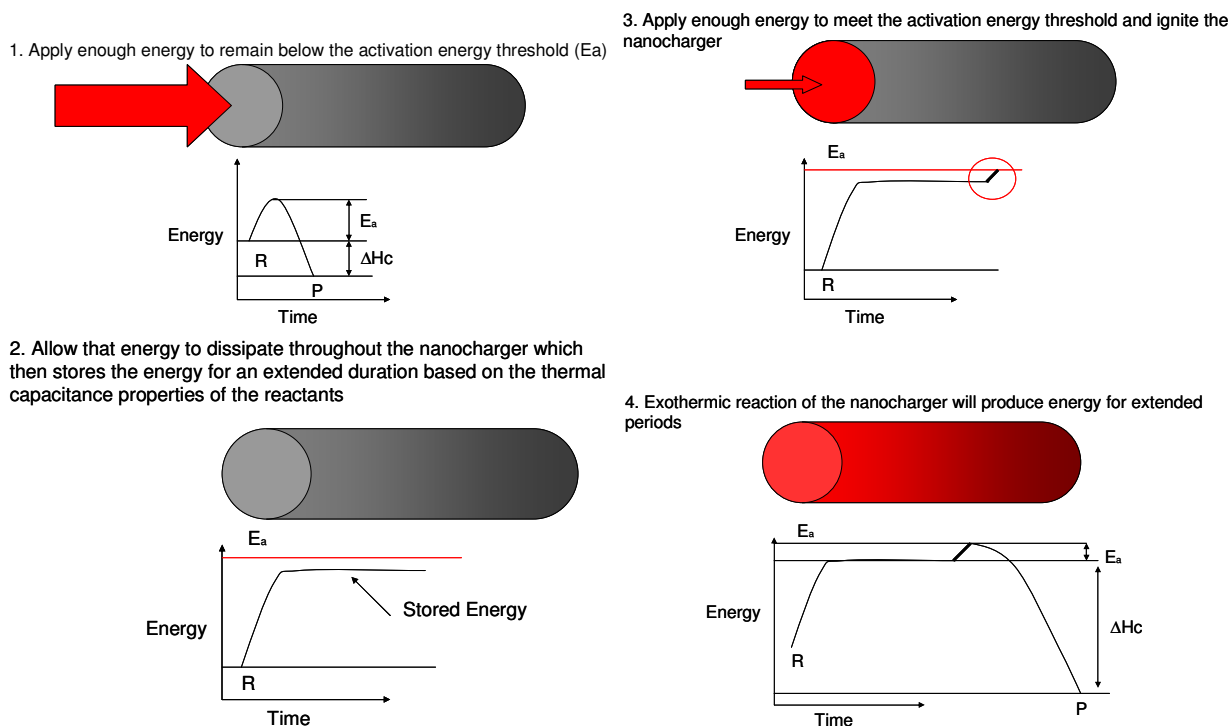


Figure 12. A concept sketch on how mildly energetic high heat capacitance formulations could be used to store thermal energy and then deliver chemical energy on demand.