REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
30-10-2015	Final Report	1-Aug-2014 - 31-Jul-2015

4. TITLE AND SUBTITLE
Final Report: Diagnostics for the Analysis of Surface Chemistry Effects on Composite Energetic Material Reactions

5a. CONTRACT NUMBER
W911NF-14-1-0417

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611103

6. AUTHORS
Michelle Pantoya

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Texas Technical University
Box 41035
349 Admin Bldg
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)
65092-EG-RIP.5

12. DISTRIBUTION AVAILIBILITY 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 contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
The objective of this grant is to purchase a coupled diagnostic system that will enable high resolution measurements of heat flow and phase change allowing chemical kinetic modeling of surface chemistry using an advanced DSC – TGA via simultaneous thermal analysis (STA). This diagnostic couples with existing Quadrapol Mass Spectrometer (QMS) that enables gas species identification in-situ equilibrium reaction. This system is also coupled with state-of-the-art IR imaging technology that enables nanosecond integration time and micron scale resolution to resolve the early stages of localized energy build up leading to ignition

15. SUBJECT TERMS
Differential Scanning Calorimetry; Reaction Kinetics; Quadrapol Mass Spectrometry; Thermal Gravimetric Analysis; Infrared Imaging; Combustion; Aluminum Particles

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Michelle Pantoya
UU	UU	UU	UU		19b. TELEPHONE NUMBER 806-834-3733

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

Report Title

Final Report: Diagnostics for the Analysis of Surface Chemistry Effects on Composite Energetic Material Reactions

ABSTRACT

The objective of this grant is to purchase a coupled diagnostic system that will enable high resolution measurements of heat flow and phase change allowing chemical kinetic modeling of surface chemistry using an advanced DSC – TGA via simultaneous thermal analysis (STA). This diagnostic couples with existing Quadrapol Mass Spectrometer (QMS) that enables gas species identification in-situ equilibrium reaction. This system is also coupled with state-of-the-art IR imaging technology that enables nanosecond integration time and micron scale resolution to resolve the early stages of localized energy build up leading to ignition.

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)

Received		Paper
10/29/2015	3.00	Evan Vargas, Michelle L. Pantoya, Mohammed A Saed, Brandon L Weeks. Advanced Susceptors for Microwave Heating of Energetic Materials, Materials and Design, (10 2015): 47. doi:
10/29/2015	1.00	Jena McCollum, Michelle L. Pantoya, Scott T. Iacono. Activating Aluminum Reactivity with Fluoropolymer Coatings for Improved Energetic Composite Combustion, ACS Applied Materials & Interfaces, (08 2015): 0. doi: 10.1021/acsami.5b05238
10/29/2015	2.00	Billy Clark, Jena McCollum, Michelle L. Pantoya, Ronald J. Heaps, Michael A. Daniels. Development of flexible, free-standing, thin films for additive manufacturing and localized energy generation, AIP Advances, (08 2015): 0. doi: 10.1063/1.4928570
10/30/2015	4.00	Billy Clark, Michelle L Pantoya, Emily M Hunt, Trent J Kelly, Benton Allen, Ronald J Heaps, Michael A Daniels. Synthesis and Characterization of Flexible, Free-Standing Energetic Thin Films, Surface & Coatings Technology, (10 2015): 0. doi:
TOTAL:		**4**

Number of Papers published in peer-reviewed journals:

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

Received		Paper
TOTAL:		

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. Padhye, R., Pantoya, M.L., Examining aluminum-PTFE Surface Reactivity, Combustion Institute Meeting, Cincinnati, Ohio, May 2015.
2. Vargas, E., Pantoya, M.L., Saed, M., Weeks, B., The influence of carbon based susceptors on microwave heating of TNT, Fall Materials Research Society (MRS) Meeting and Exhibit, Boston, MA, November 2014.
3. Vargas, E., Pantoya, M.L., Saed, M., Weeks, B., Influence of Shape on Carbon Based Susceptors on Microwave Heating of TNT, 9th US. National Combustion Meeting, Cincinnati, Ohio, May, 2015.
4. Cano, J., Kappagantula, K., Pantoya, M., Combustion Performance Improvement of Energetic Thin Films Using Carbon Nanotubes, 2015 Texas Tech University Undergraduate Research Conference, Lubbock, TX April 2015.
5. McCollum, J., Cox, J., Pantoya, M.L., Investigating fuel size effects on thermal properties of aluminum combustion, Texas Tech University Undergraduate Research Conference, Lubbock, TX April 2015.

Number of Presentations: 5.00

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

Received Paper

TOTAL:

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

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

Received Paper

TOTAL:

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

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

M. Pantoya's Army research was featured in Discovery Channel Daily Planet "Green Ammunition" and aired internationally in 2014. This was a 15 minute segment. M. Pantoya was also featured as Dr. Michelle The Engineer on PBS Kids introducing children to engineering. These are a series of 5 short (30-second) segments aired between PBS Kids programming throughout the Texas Panhandle region. M. Pantoya received recognition by the YWCA in 2015 with the Women of Excellence award in Science. M. Pantoya received the Outstanding Researcher Award from TTU in 2015.

Graduate Students

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

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: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

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:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

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 0.00

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:..... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

The application of the diagnostics purchased with this grant will continue to be and has already been shared with many scientists and researchers at ARL and other DoD labs. These individuals are all listed in the attached final report. The IR imaging diagnostic has also been used for microwave heating of energetic materials with work scoped defined as per the interests of AFRL Eglin AFB, and Dr. Maqsood Mohammad was the contact. They were very interested in the shape of Al particles and their respective electromagnetic absorption. They currently uses now a similar diagnostic for classified work.

The twenty sample carrier DSC-TGA has now been requested by many at ARL and the data created by the QMS has become of interest too. This diagnostic will have an impact in future DoD work.

Project Summary - Grant # W911NF14-1-0417
(Final Report: September, 2014 – October, 2015)

Diagnostics for Analyses of Surface Chemistry Effects on Composite Energetic Material Reactions

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

Objective

The objective of this grant is to purchase a coupled diagnostic system that will enable high resolution measurements of heat flow and phase change allowing chemical kinetic modeling of surface chemistry using an advanced DSC – TGA via simultaneous thermal analysis (STA). This diagnostic is coupled with state-of-the-art IR imaging technology that enables nanosecond integration time and micron scale resolution to resolve the early stages of localized energy build up leading to ignition.

Approach

(1) Purchase a FLIR SC 8243 high-speed IR camera that will be used to image transient thermal behavior of energetic materials at frame rates as high as 100,000 frames per second (500 ns integration time) and a NETZSCH STA 449 Jupiter that will allow for consistency and efficiency with its automatic 20 sample changer.
(2) Together these systems will enable a multi-dimensional understanding of the effect of surface reactions between the alumina passivation shell surrounding aluminum particles and any halogenated oxide inducing reaction with alumina on the overall composite's thermal combustion performance.
(3) Design experiments that will enable an understanding the fundamental chemistry associated with solid energetic material combustion.

Relevance to Army

- The FLIR SC 8243 will enable transient thermal data from two dimensional perspectives. The data will resolve the influence of surface interactions on energy build up. The instrumentation can be used on various Army supported thermite combustion research also to establish fundamental reactivity mechanisms for a variety of energetic materials.
- The NETZSCH STA 449 will provide new information on reaction kinetics and gas phase speciation from energetic material reactions. The 20 sample carrier will enable multiple experiments and testing in a single loading, this will save extensive time and provide more accurate data.
- The coupled systems provide a new multi-dimensional understanding of the effect of surface reactions between the alumina passivation shell surrounding aluminum particles and any halogenated oxide inducing reaction with alumina on the overall (i.e., macroscopic) combustion performance.
- Results obtained from this study will have a dramatic impact on the SAFE handling and use of energetic materials in addition to providing a significant understanding of the thermal response, ignition sensitivity as well as energy transfer.

Accomplishments for Reporting Period

1. Purchase of the NETZSCH STA 449 Jupiter (DSC-TGA) to resolve reaction kinetics under equilibrium conditions. Images of this instrumentation are included in **Fig. 1**. Sample data is also included in **Fig. 2**. This instrumentation is coupled with our existing FTIR and our quadraopol mass spectrometer (QMS) for resolution of gas species during equilibrium analysis. The new STA is used has been used consistently since purchased in Oct. 2014 and is a true asset to our lab and capabilities.
2. Identified key features in the NETZSCH STA 449 needed for the aluminum-fluorine reactions. These include: the temperature range has been increased from -120:1600°C to -150:2400°C, increasing the capabilities of studying elements like boron which has a melting point of 2076°C. Also, improving inert environment studies requires improved vacuum capabilities and the proposed equipment allows vacuum evacuations down to 10-4 mbar in comparison to the current 10-2 mbar. The resolution has improved to 1µg and the updated hardware and software add another dimension to the assessment capabilities. See Fig. 1 for many images of this system.
3. Purchase of the FLIR SC 8303 high speed IR camera to measure two-dimensional transient thermal images. Images of this system are provided in **Fig. 3**. The infrared camera operates in the mid-wavelength region that spans a band of wavelengths from 3-5 µm. In a typical experiment, the viewing area of both the sample and holder is set at a 640 X 360 pixel window frame size. The integration time is set to 2.1 ms with an acquisition rate of 15 frames per second. That is: 230,400 discrete temperature measurements are made throughout the field of view every 2.1 ms. Emissivity of a sample is determined by referencing a known emissive source and then calibrated into the infrared camera. Sample data from this instrument are presented in **Fig. 4** for the analysis of susceptors in TNT composites.
4. Identified key features necessary for aluminum and fluorine reactivity including: first, the resolution improvement in comparison to our existing IR camera is over 200%! The high resolution is critically important for resolving thermal energy 'hot-spots' that spur ignition and also critical to resolving exothermic surface chemistry that can manifest prior to ignition. Second, the ultra-high speed diagnostic will image transient thermal behavior at frame rates as high as 100,000 frames per second (e.g., 500 ns integration time). This temporal resolution is essential for capturing the early stage thermal buildup associated with pre-ignition and far surpasses our existing ability to monitor functionally at only 100 microsecond resolution. Third and most important, an on-board calibration system that enables direct radiance to temperature measurements from -20 up to 500 °C and up to 2000 °C with an additional calibration source (within the camera). This will eliminate the constant need for re-calibration using an external black body source (that consumes over 5 square feet of lab space) coupled with multiple materials of varying emissivity and unique calibrations associated with small variations in experimental setup. With the new instrumentation, the onboard calibration will enable significantly reduced labor hours and errors associated with experimental operation.

Collaborations and Technology Transfer

- Mr. Mark Boccella, FLIR-Indigo Systems
- Drs. Barry Homan, Kevin McNesby, Brad Forch (ARL)
- Drs. John Schmidt, Stephen Howard, Richard Beyer (ARL)
- Drs. Barry Homan, Kevin McNesby, Brad Forch (ARL)
- Drs. John Schmidt, Stephen Howard, Richard Beyer (ARL)
- Mr. Todd Dutton and Eric Bukowski (ARL)
- Dr. Scott Iacono (Air Force Academy)
- Drs. Ron Heaps, Michael Daniels and Dan Prentice (INL)
- Drs. Shawn Stacy & Christopher Apblett (SNL)
- Dr. Benjamin Shaw (Univ. of California, Davis)
- Dr. Keerti Kappagantula (Ohio University)
- Drs. Emily Hunt & Oliver Mulamba (West Texas A&M)
- Dr. Valery Levitas (ISU)
- Dr. Santanu Chadhuri (WSU)

- Drs. John Granier and Dennis Wilson (EMPI, Inc.)
- Drs. Charles Crane & Cory Farley (LANL)
- Dr. David Irvin (Systems & Materials Research Corp.)
- Dr. Christopher Junk (DuPont)
- Drs. Carol Korzeniewski & Adelia Aquino (Texas Tech, Chemistry Dept.)

Resulting Journal Publications during Reporting Period

1. McCollum, J., Pantoya, M.L., Iacono, S., Activating Aluminum Reactivity with Fluoropolymer Coatings for Improved Energetic Composite Combustion, *Applied Materials and Interfaces*, 33(7), 18742-18749, 2015.
2. Clark, B.R., McCollum, J., Pantoya, M.L., Heaps, R., Daniels, M.A., Development of Flexible Free Standing Thin Films for Additive Manufacturing and Localized Energy Generation, *AIP Advances* 5(8), 087128, 2015.
3. Bello, M., Pantoya, M.L., Kappagantula, K., Wang, W.S., Vanapalli, S.A., Irvin, D.J., Wood, L.M., Reaction Dynamics of Rocket Propellant with Magnesium Oxide Nanoparticles, *Energy & Fuel*, 29(9), 6111-6117, 2015.
4. Vargas, E., Pantoya, M.L., Saed, M.A., Weeks, B.L., Advanced Susceptors for Microwave Heating of Energetic Materials, *Materials & Design*, 90, 47-53, 2016.
5. Smith, D., Pantoya, M.L., Effect of Nanofiller Shape on Thermal Conductivity of Fluoropolymer Composites, *Composites Science and Technology*, 118, 251-256, 2015.
6. Clark, B.R., Pantoya, M.L., Hunt, E.M., Kelly, T.J., Allen, B.F., Heaps, R.J., Daniels, M.A., Synthesis and Characterization of Flexible, Free-Standing, Energetic Thin Films, *Surface Coatings and Technology*, In Press 2015.
7. McCollum, J., Pantoya, M.L., Iacono, S., Catalyzing Aluminum Particle Reactivity with Fluorine Oligomer Surface Coating for Energy Generation Applications, *Journal of Fluorine Chemistry*, In Press 2015
8. Padhye. R., McCollum, J., Pantoya, M.L., Korzeniewski, C., Examining hydroxyl – alumina bonding toward aluminum reactivity, *Journal of Physical Chemistry C*, In Review October 2015.

Graduate Students Involved During Reporting Period

- Jena Mccollum (PhD)
- Evan Vargas (PhD)
- Billy Clark (PhD)
- Dylan Smith (MS)
- Richa Padhye

Awards, Honors and Appointments

M. Pantoya's Army research was featured in Discovery Channel Daily Planet "Green Ammunition" and aired internationally in 2014. This was a 15 minute segment. M. Pantoya was also featured as *Dr. Michelle The Engineer* on PBS Kids introducing children to engineering. These are a series of 5 short (30-second) segments aired between *PBS Kids* programming throughout the Texas Panhandle region. M. Pantoya received recognition by the YWCA in 2015 with the Women of Excellence award in Science. M. Pantoya received the Outstanding Researcher Award from TTU in 2015.

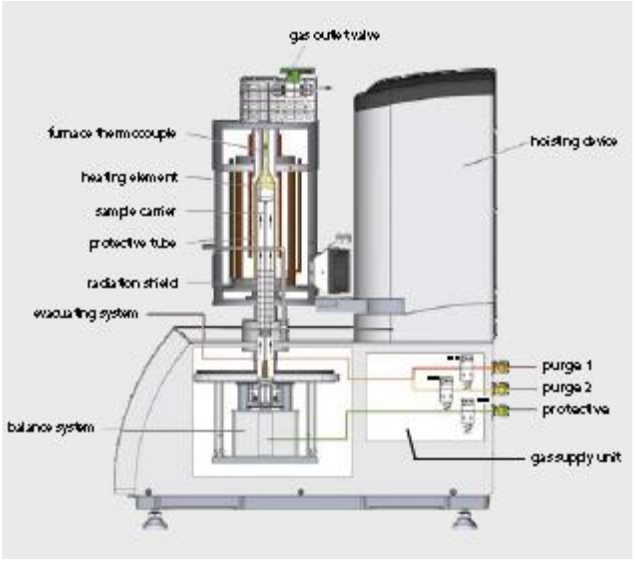


Figure 1. Twenty sample carrier for individually programmable analysis in the STA. Image of the DSC-TGA and schematic of instrumentation. These images are curtesy of NETZSCH.

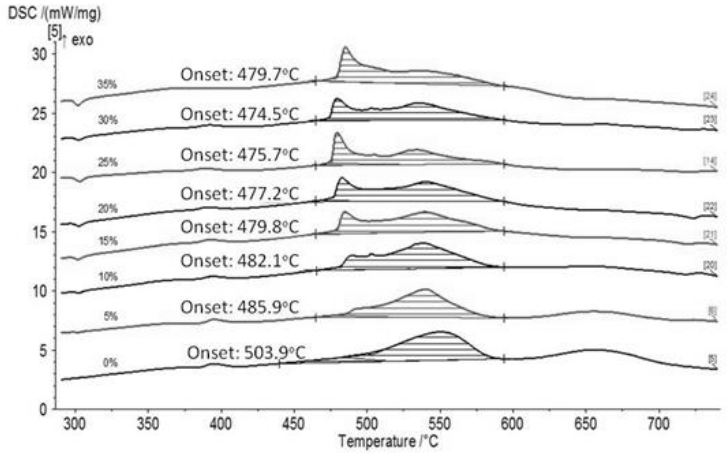
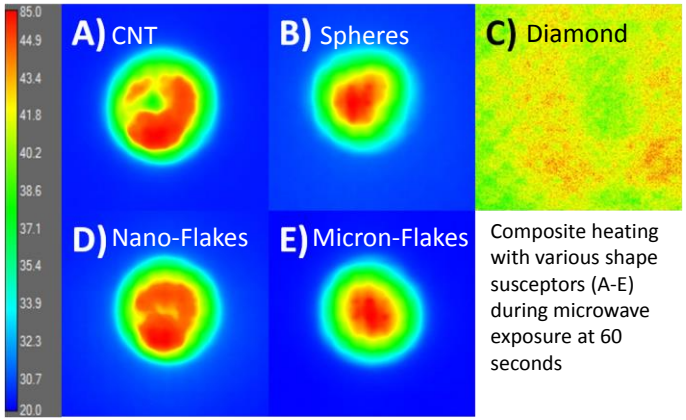


Figure 2. Heat flow results from new DSC on energetic films with varying $KClO_4$ concentrations in air; experiments performed at a heating rate of 10 KPM. Reactivity shifts to lower onset with increasing $KClO_4$ concentration. Gradual increase in initial peak is indicative of the silicone binder reacting with $KClO_4$. **[1]**

Figure 3. FLIR SC 8303 infrared camera. Image curtesy of FLIR – Indigo Systems Inc.



Composite heating with various shape susceptors (A-E) during microwave exposure at 60 seconds

Figure 4 A. Still frame IR images of a 1 cm diameter TNT pellet seeded with carbon particle susceptors of different shape exposed to microwave radiation at 60 seconds. **B.** Transient average temperature for each susceptor. **[6]**