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Major Goals: The main goal is to enhance aluminum reactivity through understanding surface exothermic kinetics that facilitate combustion. To accomplish this goal, this project examines surface reactions of aluminum particles with various halogen containing oxidizers (i.e., fluorine and iodine) as well as ignition and combustion properties affected by these surface reactions. The surface reactions are triggered by a halogen species, such as fluorine in fluoropolymers or iodine or chlorine oxidizing salts or binders. The objective is to understand the reaction kinetics of halogens with the alumina passivation shell surrounding aluminum particles, then use this understanding to design formulations that show greater reactivity. Our focus is on three areas of research including: (1) developing mechanistic understanding of reaction pathways that promote surface reactions; (2) analyzing and modeling Al combustion for ignition and energy propagation; and, (3) synthesizing and characterizing novel formulations that capitalize on the surface reactions.

Specific research questions: (1) How does surface chemistry affect oxidation, chemical energy generation, and energy release rates; (2) What reaction pathways are needed to promote the surface reactions; (3) How can the alumina surface be manipulated to enhance surface reactions; (4) What reaction kinetics accelerate oxidation rates and how can those kinetics be exploited to synthesize new formulations; (5) What controlling mechanisms and modes of energy transport are dominant and how do those mechanisms vary with oxidizer.

Accomplishments: See Figures in Attachment.

We are identifying key reaction pathways that promote surface chemistry and enhance overall Al reactivity. To harness greater power from Al combustion one approach is to chemically transform the alumina (Al_2O_3) passivation layer surrounding the Al core particle by exploiting surface reactions via wet chemistry. We identified key parameters affecting interfacial chemistry on Al particles specific to the formation of aluminum iodate hexahydrate (AIH). Experiments were designed using a range of diagnostics including XRD, XPS, TEM, DSC, TGA, LASEM, and more. Results showed AIH formation is facilitated on hydrated alumina surfaces and specifically, AIH formation is linked to removal of terminal OH bonds. In fact, a systematic approach was designed to synthesize pure AIH from $Al(OH)_3$ powder that was immersed in iodic acid solution. Figure 1 shows an SEM image of pure AIH crystals along with the X-ray diffraction pattern. The AIH crystals are highly reactive as an oxidizer when combined with metal fuel particles. In fact, Fig. 2 shows flame speeds measured for mixtures of AIH and Al compared with AIH that is coated on Al particles. As a coating, the AIH decomposes at low temperatures such that diffusion reactions are accelerated and the flame speeds correspondingly increase. This understanding informs new synthesis strategies that are tailored to preparing Al particles with purposefully hydrated surface coatings (see Fig. 3 concept sketch). The hydration layer will be used in future work to catalyze specific reactions that will transform the aluminum particle's shell chemistry toward altered (enhanced) reactivity.

We explored alternative methods for altering the shell chemistry that included mitigating the alumina shell using different gas discharge plasmas leading to Al particles with a thinner shell. This work was done by Ms. Kelsea Miller (TTU) at Aberdeen Proving Ground (APG) using Dr. Chi-Chin Wu's dielectric barrier discharge (DBD) plasma apparatus (see Fig. 4) at APG. Two gas discharge plasmas were examined: helium (He) and argon (Ar), and both induced thinning of the Al shell (Fig. 5). Interestingly, the Ar plasma promoted significant hydration of the Al particle surface by altering the alumina into a metastable state that readily absorbs water. Fig. 6 shows TGA data that revealed significant mass loss associated with the hydrated Ar plasma treated Al particles and XRD data analysis with Rietveld refinement indicated about 50% of the Ar plasma treated particles became a hydrated form of alumina, specifically boehmite: AlO(OH). This form of hydrated alumina is actually the most stable and does not readily transform into AIH.

All plasma treated Al particles were then further processed in an iodic acid solution. The results showed all the plasma treated Al particles produced many iodine-containing species on the surface, including: HIO3, HI3O8, and AIH. Figure 7 shows TEM images of the Al particle surfaces decorated with iodine-species and Fig. 8 shows the concentration of different iodine species detected via XRD data analysis using Rietveld refinement. Figures 7 and 8 reveal two very interesting features: (1) When Al particles are plasma treated to induce shell thinning, the outer hydration layer is reduced. With the reduction of a hydration layer when the particles are immersed in iodic acid, the iodine species that form are more localized on the surface. Specifically, the iodine species decorate the particles as opposed to fully coat the particle as seen for non-plasma treated Al particles (Fig.7). (2) For the wet-chemistry conditions studied here, the iodine species decorating plasma treated Al particles have various composition (i.e., HIO3, HI3O8, and AIH) whereas when non-plasma treated Al particles were immersed in iodic acid, 100% of the transformation is to AIH. The differences in chemical composition of surface species may be attributed to the wet chemistry conditions. Specifically, the plasma treated particles were not immersed in the iodic acid long enough to allow complete transformation to AIH. Energetic tests utilizing laser-induced air shock for energetic materials (LASEM) show significantly enhanced energy release rates at the μs timescale for plasma treated nAl decorated with iodine species (Fig. 9). The LASEM tests indicate that there is great potential for using this methodology to prepare Al particles for further chemical treatment and show that chemical treatment of Al particles significantly impacts their reactivity at time scales relevant to a detonation event.

In another study, we used pure AIH synthesized in our lab (see Fig. 1) in reactions with metal oxides [4]. This study showed that AIH reacts with metal oxides exothermically to form metal iodates, in-situ of the reaction. The significance of this understanding is that upon AIH decomposition, metal iodates are actually more stable than the metal oxides and metal iodates are good oxidizers for fuel particle reactions. So, by forming metal iodiates in-situ a reaction, AIH contributes towards increasing the reaction pathways for Al combustion in a mixture with CuO (e.g., Al + AIH, Al + CuO, Al + CuIO3). Also, the formation of metal iodates is exothermic such that the AIH + Metal Oxide reactions actually contribute exothermic energy to the overall reactivity. Further tests are on-going to understand these ternary reactions.

We have started to extend our research on surface chemistry to other fuel particles. Specifically, we started studying magnesium (Mg) particles because of its similar properties compared to Al (e.g., similar core-shell structure, similar melting temperatures of core and shell, similar core-shell strength properties). Magnesium particles are surrounded by a complex hydroxide shell composed of an inner layer of magnesium oxide (MgO) and outer layer of magnesium hydroxide (Mg(OH)2). This hydrated structure shows promise for surface chemistry alterations of Mg, but we started with a more basic analysis of surface chemistry that is a function of particle size. As Mg particles approach the nanoscale, the thick oxide shell (e.g., 22 nm) becomes an appreciable portion of the overall powder. In this study [5], the reactivity of 800 nm Mg particles (nMg) was compared to 44 μm Mg particles (μMg) when combined with Perfluoropolyethyer (PFPE), providing both fluorine and oxygen for Mg reactions. Experiments were performed at slow heating rates (10°C/min) and separate experiments were performed at fast heating rates (6.0 x 105 °C/min). For nMg powders, the outer Mg(OH)2 surface layer dehydrates at low temperatures (313°C) creating highly reactive sites for surface oxidation reactions in the condensed phase leading to a higher conversion of Mg(OH)2 to MgO and greater consumption of Mg through oxidation reactions. For μMg, higher Mg(OH)2 dehydration temperatures (498°C) stabilize μMg particles and the bulk of reactions occur at elevated temperatures and in the gas phase producing higher MgF2 concentrations. Under high heating rate conditions, MgF2 formation is favored over MgO formation for both particle sizes owing to the high reaction temperatures that promote gas phase reactions. The results from this study are summarized in a single graphic (Fig. 11) and suggest that surface chemistry induced by an iodic acid solution will be a strong function of the particle size, and could significantly affect the smaller, nanoscale particles owing to the higher contribution of Mg (OH)2. The next step in this work is to use pure Mg(OH)2 particles in iodic acid solution to synthesize a magnesium-iodate-hydrate crystal structure.

Training Opportunities: In the Pantoya research group the following PhD and MS students worked on this project (all US citizens): Mr. Loudon (Lee) Campbell (PhD), Ms. Kelsea Miller (PhD), Ms. Shancita Islam (PhD), Ms. Renita Walzel (MS), Connor Woodruff (PhD), Charles (Luke) Croessmann, Colten Cagle, and Mr. Ryan Bratton (PhD). Lee, Kelsea, Ryan and Shancita are anticipated to graduate in 2021, and Renita graduated with a MS degree in May 2019 and is now employed by Los Alamos National Laboratory working in energetic materials science. Ryan's dissertation focus is imaging diagnostics and he has contributed to diagnostic developments that enable visualization of highly luminescent reactions. He has received extensive training on how speed imaging from Phantom in Wayne, NJ and has prepared instructional seminars for the other graduate students in our group. Kelsea has been working for two summers (2018 and 2019) at Aberdeen Proving Ground with Drs. Chi-Chin Wu and Jennifer Gottfried. Her work is focused on synthesizing AIH on the surface of Al particles using plasma treatment techniques. She developed extensive materials science skills while at APG including TEM and spectroscopy analysis (working with Dr. Scott Walck) and XRD. She has transferred these skills to the other graduate students in our group via training seminars. Ms. Shancita Islam has also been working on surface chemistry and AIH synthesis and has been trained at Texas Tech on various diagnostics including DSC-TGA, XPS, XRD, SEM and TEM. She assists other students in performing experiments and has taught them how to analyze some data sets (i.e., XPS data). Mr. Lee Campbell's research is focused on 3D printing of energetic materials. He is working closely with Dr. Brian Fuchs at Picatinny Arsenal on developing the capabilities to print controlled density gradients.
Both Lee and another PhD student, Alan Williams also spent 1 week at the Advanced Photon Source (APS) at Argonne National Laboratory to learn and perform experiments using Dynamic Compression Sector. This training will benefit our ARO program by expanding our characterization capabilities for aluminum particles under shock ignition conditions.

All of the students working on this project have been trained on the safe handling and use of energetic materials as well as trained on the state of the art diagnostic equipment used throughout our laboratory.

Each student has also participated in various professional meetings throughout the year including the Applied Physics Symposium and the Materials Research Symposium.
Students have also been working with and mentored by Army lab scientists. Ms. Kelsea Miller spent June-August in 2018 and 2019 at Aberdeen Proving Ground working with Dr. Chi-Chin Wu and Mr. Loudon (Lee) Campbell spent June-August 2018 and 2019 at Picatinny Arsenal working with Dr. Brian Fuchs. These collaborative relationships continue remotely. Ms. Shancita Islam has also worked closely with Dr. Chi-Chin Wu and Scott Walck. Finally, Ms. Renita Walzel worked at Los Alamos National Laboratory June-August 2018 with Dr. Alex Muller on research directed at using our formulations for additive manufacturing. She is now employed as a staff scientist at LANL.

Two undergraduate research assistants who worked on this project are now graduated with BS degree and enrolled as graduate students: Colt Cagle and Charles (Luke) Croessmann. Colt is an excellent machinist and has assisted in the design and fabrication of our high velocity impact ignition system that will be used to characterize the reactivity. Luke and Colt have been working closely this past summer on designing new experimental diagnostics for characterizing Al and AIH combustion.

Results Dissemination: Results were disseminated to a broad audience in several ways: (1) presentations at conferences and meetings throughout the year; (2) journal publications; (3) visits with key researchers at military and national labs, as well as industry. These visits were either at Texas Tech University or their respective institution. The following highlights specific activities.

- Presentations at conferences and meetings. Below summarizes presentations or posters disseminated at various conferences.

1. Walzel, R.K., Pantoya, M.L., Aluminum particle reactivity as a function of alumina shell structure: amorphous versus crystalline, 11th US National Combustion Institute Meeting, March 24-27, 2019.
2. Wu, C.-C., Gottfried, J.L., Walck, S.D., Miller, K. K., Pesce-Rodriguez, R.A., Pantoya, M.L., Making Energetic Aluminum Particles As Novel Energetics with Plasmas, 66th JANNAF Propulsion/ 49th Combustion Proceedings, Dayton, OH, June 3-7, 2019.
3. Pantoya, M. L., Surface Chemistry Promoting Energetic Material Combustion, Invited Seminar, Rutgers, NJ, Feb. 2020.

- Archival journal publications. The publications this reporting period from our ARL research and are included in attached pdf file are summarized here:
- Shancita, I., Campbell, L.L., Wu, C.C., Walck, S.D., Aquino, A., Tunega, D., Pantoya, M.L., The effect of hydration on promoting oxidative reactions with aluminum oxide and oxyhydroxide nanoparticles, J of Phys Chem C 123, 15017-15026, 2019.
- Kalman, J., Smith, D.K., Miller, K.K., Bratton, K.R., Pantoya, M.L., A strategy for increasing the energy release rate of aluminum by replacing the alumina passivation shell with aluminum iodate hexahydrate (AIH), Comb Flame 205, 327-335, 2019.
- Miller, K., Shancita, I., Bhattacharia, S., Pantoya, M.L., Atmospheric Pressure Plasma Surface Treatment on Aluminum Particles and Surface Reactions Altering the Alumina Shell Chemistry, Submitted to J of Phys Chem C, August 2020.
- Shancita, I., Miller, K. K., Silverstein, P.D., Kalman, J., Pantoya, M.L., Synthesis of Metal Iodates from Aluminum Iodate Hexahydrate Salt, RSC Advances 10, 14403-14409, 2020.
- Shancita, I., Vaz, N., Fernandes, G., Aquino, A., Tunega, D., Pantoya, M.L., Regulating Magnesium Combustion Using Surface Chemistry and Heating Rate, Submitted to J of Phys Chem C, August 2020.
- Bratton, K.R., Woodruff, C., Campbell, L.L., Heaps, R.J., Pantoya, M.L., A Closer Look at Determining Flame Speeds with Imaging Diagnostics, Optics and Lasers in Engineering 124, 105841, 2020.
- Campbell, L.L., Hill, K. J., Smith, D.K., Pantoya, M.L., Thermal Analysis of Microscale Aluminum Particles Coated with Perfluorotetradecanoic (PFTD), J Thermal Anal and Calorimetry, 2020.
- Shancita, I., Woodruff, C., Campbell, L.L., Pantoya, M.L., An Iodine Rich Binder for Energetic Material Applications, Therm Acta, 2020.
- Walzel, R. K., Levitas, V.I., Pantoya, M.L., Aluminum particle reactivity as a function of the alumina shell structure: amorphous versus crystalline, Powder Technology, 374, 33-39, 2020.

Honors and Awards: M. Pantoya received a TTU Outstanding Research Award in May, 2020.
K. Miller (PhD) and Luke Croessmann (PhD) were awarded internship appointments at Aberdeen Proving Ground. K. Miller was mentored by Dr. Chi-Chin Wu and L. Croessmann was mentored by Dr. Jennifer Gottfried. L. Campbell (PhD) was awarded an internship appointment at Picatinny Arsenal ARDEC as an Engineering Intern (2020).

Protocol Activity Status:

Technology Transfer: We have not filed patent applications or inventions, licenses. We have had significant interactions with DoD laboratories - we work with our collaborators at Picatinny Arsenal (ARDEC) and Aberdeen Proving Ground nearly daily via email or phone. These interactions are briefly summarized here.

- Drs. Brian Fuchs (ARL, ARDEC, Picatinny Arsenal), Andrew Ihnen (NAWC-WD), Didier Montaigne (AFRL, Eglin AFB) – We are leveraging our ARO project on Al fuel particles with on-going additive manufacturing development at Picatinny Arsenal. Mr. Loudon Lee Campbell is the TTU student working on this project that includes the design of a variable density printing system. The goal of the printing system is to process energetic formulations into tailored architectures with density gradients. Mr. Campbell’s dissertation will be focused on the design and development of the 3D printing system.
- Drs. Chi-Chin Wu, Jennifer Gottfried, Rose Pecase-Rodrigez, Scott Walck, Kevin McNesby (ARL, APG) – We have been collaborating with Dr. Wu on plasma surface treatment of Al particles. Dr. Chi-Chin was awarded an ARL external collaboration initiative (ECI) to help support further plasma surface treatment studies on fuel particles. Ms. Kelsea Miller is the TTU student working on this project and has worked at APG in the summer of 2018 & 2019. She processed the plasma treated Al particles in iodic acids to develop an AIH surface coating and Dr. Gottfried studied these samples using LASEM. We have been working with Dr. Gottfried to streamline her LASEM diagnostic in order to accurately quantify energy release behaviors using small samples of material. Scott Walck has been working with us on TEM analysis of surface and interface properties of aluminum particles. Dr. McNesby donated a high speed camera filter that will enable us to more accurately resolve high temperatures from data collected using our Phantom high speed color camera. We communicate with Kevin frequently as we are both working towards optimizing the temperature measurement diagnostic approach.
- Dr. Dylan Smith (Eglin AFB) –continues to engage in helpful discussions with us promoting our understanding of AIH formation and wet chemistry approaches we can apply to altering the surface chemistry on fuel particles.
- Dr. Robert Carl Brothers (NSWC-IHEODTD) –is a synthetic chemist that has been developing iodine-fluorine containing binders. He has shared some of his materials with us and we are studying the reactive behaviors with aluminum.
- Dr. Alexandra Reinert (NSWC-IHEODTD) has also been working with us to better understand and characterize reactivity under high velocity impact and penetration conditions. The focus of this work is on reactive material projectiles designed to optimize performance for specific applications.
- Dr. Igor Altman (NAWCWD) has been working with us closely to resolve heat transfer mechanisms at the surface of fuel particles, specifically focusing on the energy accommodation coefficient.

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Participant: Adelia Aquino
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Project Contribution:
National Academy Member: N

Participant Type: PD/PI
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Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

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National Academy Member: N

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National Academy Member: N

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Article Title: Surface engineered nanoparticles dispersed in kerosene: The effect of oleophobicity on droplet combustion
Authors: Michael N. Bello, Kevin J. Hill, Michelle L. Pantoya, Richard Jason Jouet, Jillian M. Horn
Keywords: aluminum, combustion, liquid propellants, oleophobicity, hydrophobicity
Abstract: Liquid propellants benefit from solid particle additives that can optimize combustion performance by promoting phase change heat transfer. In this study, aluminum (Al) nanoparticles with and without self- assembled monolayer surface functionalization were combined with kerosene to examine the changes in droplet regression behavior associated with manipulating particle surface chemistry. Aluminum nanopar- ticles were coated using a long-chain perfluorinated carboxylic acid as the surface binding moiety to induce an oleophobic surface. The resulting particles are thus comprised of self-assembled monolayers of perfluorohexadecanoic acid (PFHD) (C 15 F 31 COOH) around the alumina (Al 2 O 3) shell encapsulating the Al core. The PFHD serves many functions including altering particle wettability and acting as a surfactant that facilitates a stabilized dispersion of particles in kerosene.
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Article Title: Replacing the Al2O3 Shell on Al Particles with an Oxidizing Salt, Aluminum Iodate Hexahydrate. Part II: Synthesis
Authors: Dylan K. Smith, Daniel K. Unruh, Michelle L. Pantoya
Keywords: aluminum, iodic acid, aluminum iodate hexahydrate, combustion, metal fuels
Abstract: The main reaction mechanism that replaces the Al2O3 passivation layer on Al nanoparticles with an energetic AIH salt is demonstrated. The reaction mechanism is pH dependent and utilizes electrostatic forces that occur between the Al2O3 passivation layer and free hydrogen atoms (H+) in solution. When Al particles are added to highly acidic solutions, free H+ polarize the Al?O bonds in Al2O3, resulting in the formation of H2O and free Al3+ cations that are complexed by water molecules and exist as [Al(H2O)6]3+ in aqueous solutions. The concentration of AIH is limited by the amount of [Al(H2O)6]3+ that forms from the polarization reaction between free H+ and the initial Al2O3 concentration. The proposed mechanism describes a stoichiometric reaction, but deviations from the stoichiometric reaction are expected with varying equivalence ratios (ER). The polarization mechanism is confirmed by measuring deviations in concentration of final AIH mixtures as a function of ER.
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Article Title: Replacing the Al2O3 Shell on Al Particles with an Oxidizing Salt, Aluminum Iodate Hexahydrate. Part I: Reactivity
Authors: Dylan K. Smith, Daniel K. Unruh, Chi-Chin Wu, Michelle L. Pantoya
Keywords: aluminum, iodic acid, surface chemistry, aluminum iodate hexahydrate, combustion, metal fuels
Abstract: Improvements in the reactivity, measured in terms of flame speed, for aluminum-based energetic mixtures are increased by a factor of 2?3 by replacing the Al2O3 passivation layer of aluminum (Al) nanoparticles with aluminum iodate hexahydrate (AIH), an oxidizing salt. The Al?AIH nanoparticles are examined under transmission electron microscopy. An AIH passivation shell surrounding the Al core particle is a more reactive composite structure than Al2O3 passivation around Al which facilitates increased reaction rates with flame speeds as high as 3200 m/s. Flame speed measurements are used to show that reaction rates in AIH mixtures are determined by the AIH/Al2O3 ratio, oxygen balance, and ?-HIO3. Further optimization of these properties will ultimately boost significant increases in the reaction rates of the energetic materials presented in this article.
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Article Title: Improving the Explosive Performance of Aluminum Nanoparticles with Aluminum Iodate Hexahydrate (AIH)
Authors: Jennifer L. Gottfried, Dylan K. Smith, Chi-Chin Wu, Michelle L. Pantoya
Keywords: aluminum fuel particles, detonation, deflagration, aluminum iodate hexahydrate
Abstract: A new synthesis approach for aluminum particles enables an aluminum core to be passivated by an oxidizing salt: aluminum iodate hexahydrate (AIH). Transmission electron microscopy (TEM) images show that AIH replaces the Al2O3 passivation layer on Al particles that limits Al oxidation. The new core-shell particle reactivity was characterized using laser-induced air shock from energetic materials (LASEM) and results for two different Al-AIH core-shell samples that vary in the AIH concentration demonstrate their potential use for explosive enhancement on both fast (detonation velocity) and slow (blast effects) timescales. Estimates of the detonation velocity for TNT-AIH composites suggest an enhancement of up to 30% may be achievable over pure TNT detonation velocities. Replacement of Al2O3 with AIH allows Al to react on similar timescales as detonation waves.
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Article Title: Discovery of Beta Phase HIO3; A Metastable Polymorph of HIO3
Authors: Dylan K. Smith, Daniel K. Unruh, Michelle L. Pantoya
Keywords: iodic acid, HIO3, polymorphs
Abstract: The ?-HIO3 polymorph, previously difficult to detect and whose existence was questioned, has been structurally characterized. The crystal structure of ?-HIO3 was solved in the same space group as ?-HIO3 (P212121); however, it was found that the unit cell axes were all different by about 1 Å. Similar to that of ? and ? phases, the unit cell contains only a single HIO3 molecule in the asymmetric unit with I-O bond lengths ranging from 1.786(5) to 1.903(7) Å. The I(V) atom is further coordinated by three oxygen atoms of neighboring acid molecules forming a distorted octahedral with a range of I-O distances (2.498(6) - 2.795(7) Å). The one structural difference that separates the ? phase from the ? and ? phases is that the hydroxyl group is bridging between two I (V) atoms, resulting in a smaller hydrogen bonding distance (O-O distance: 2.559 Å (?), 2.665 Å (?) and 2.696 Å (?)) and presumably a different crystalline energy.
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Authors: I. Shancita, Loudon Lee Campbell, Chi-Chin Wu, Adelia J.A. Aquino, Scott D. Walck, Daniel Tunega, Mi
Keywords: alumina surface chemistry, hydration, catalysis, aluminum iodate hexahydrate
Abstract: The goal of this study is to identify key parameters affecting interfacial chemistry on Al particles. As models for the surface layer of Al particles, ? aluminum oxide (?-Al2O3) and boehmite (?-AlO(OH)) nanoparticles are examined. Density functional theory calculations of dehydroxylation and dehydration energies are conducted on ?-Al2O3 and ?-AlO(OH). The calculations predict that OH bridge bonds throughout ?-AlO(OH) require similar energy to break compared with terminal OH groups abundant on the surface of ?-Al2O3 and are the most reactive sites. Experimentally, the predictions are confirmed by isolating representative surface reactions using ?-Al2O3 and ?-AlO(OH) nanoparticles suspended in an iodic acid solution to synthesize an oxidizing salt, aluminum iodate hexahydrate (AIH).
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: MRS Advances
Publication Identifier Type: DOI Publication Identifier: 10.1557/adv.2019. 159
Volume: Issue: First Page #:
Date Submitted: 8/8/19 12:00AM Date Published: 3/12/19 5:00AM
Publication Location:
Article Title: Material Characterization of Plasma-Treated Aluminum Particles via Different Gases
Authors: Chi-Chin Wu, Kelsea K. Miller, Scott D. Walck, Michelle Pantoya
Keywords: aluminum iodate hexahdrate, iodine oxidation, plasma science, aluminum particles
Abstract: This work describes exploration of mitigating the parasitic amorphous alumina (Al2O3) shell of aluminum nanoparticles (n-Al) and modifying the surface using different plasmas, leading to n-Al with thinner shell and different coatings including carbons and oxidizing salt called aluminum iodate hexahydrate (AIH), respectively. The approach exploits a prototype atmospheric non-thermal plasma reactor with dielectric barrier discharge (DBD) configuration for nanoparticle surface modifications using n-Al of 80 nm average diameter as an example. Preliminary results indicate that the amorphous Al2O3 shell surrounding the active aluminum core can be mitigated with inert plasmas by as much as 40% using either helium (He) or argon (Ar). The particle surface becomes carbon-rich with carbon monoxide (CO) / He plasmas.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: J. Appl. Phys.
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.5059423
Volume: 125 Issue: First Page #: 015102
Date Submitted: 8/8/19 12:00AM Date Published: 12/27/18 6:00AM
Publication Location:
Article Title: Photoinduced heat conversion enhancement of metallic glass nanowire arrays
Authors: Ceren Uzun, Chandrasekhar Meduri, Niloofar Kahler, Luis Grave de Peralta, Jena M. McCollum, Michel
Keywords: thermal conductivity, nanowires, aluminum
Abstract: Materials with high photo-thermal efficiency are essential in a wide variety of applications from medicine to renewable energy.Photo-thermal materials effectively absorb and convert light into heat. Nanostructures have proven to enhance absorption and heat retention owing to their large surface areas and restricted heat pathways. Here, we demonstrate that the optical absorption and heat conversion in near-infrared can be enhanced by using metallic glass nanowires whose geometry can be readily tailored through thermoplastic molding. Infrared thermography measurements and heat transport simulations reveal that the photoinduced temperature rise can be amplified by increasing the length of nanowires and decreasing the thickness of the supporting substrate.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Combustion and Flame
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.combustflame.2019.04.042
Volume: 206 Issue: First Page #: 211
Date Submitted: 8/8/19 12:00AM Date Published: 4/21/19 5:00AM
Publication Location:
Article Title: Plasma surface treatment of aluminum nanoparticles for energetic material applications
Authors: Kelsea K. Miller, Jennifer L. Gottfried, Scott D. Walck, Michelle L. Pantoya, Chi-Chin Wu
Keywords: aluminum fuel particles, detonation, deflagration, aluminum iodate hexahydrate
Abstract: This work explores a new approach to engineering the nAl surface using atmospheric argon (Ar) plasma to ac- complish two objectives: (1) reduce the nAl oxide shell thickness, and (2) synthesize AIH on the treated particle surface. Transmission electron microscopy (TEM) reveals more than 40% reduction in the oxide thickness after 10 min Ar plasma treatment. Laser-induced air shock from energetic materials (LASEM) experiments show significant energy release enhancements for the plasma-treated nAl with AIH coating (PT-nAl-AIH) compared to commercial nAl as well as untreated nAl with AIH coating (UT-nAl-AIH). The results demonstrate the potential of applying atmospheric plasma techniques to modify nAl for enhanced reactivity.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Advanced Engineering Materials
Publication Identifier Type: DOI Publication Identifier: 10.1002/adem.201801324
Volume: Issue: First Page #: 1801324
Date Submitted: 8/8/19 12:00AM Date Published: 1/15/19 6:00AM
Publication Location:
Article Title: Effects of Shear Rate during Energetic Material Processing on Reactivity
Authors: Michael A. Sweeney, K. Ryan Bratton, Connor Woodruff, Colt Cagle, Kevin J. Hill, Michelle L. Pantoya,
Keywords: additive manufacturing, rheology, aluminum, combustion
Abstract: Energetic materials are often processed at high rates of deformation as colloidal slurries and then cured. The slurries are non-Newtonian colloidal solutions that exhibit changes in microstructure with variations in applied flow. This study shows that changes to microstructure due to applied flow affect the reactivity of energetic thin films. Energetic thin films of identical composition and geometry are prepared with different applied shear rates, which produce variations in the film microstructure by segregating smaller particles toward surfaces. Results show that films exhibit significant gains in flame speed with increasing shear rate. The differences in flame speed are linked to variations in microstructure. Specifically, densification of smaller particles near a boundary promote increased flame speeds. However, when particles become segregated, larger particles tend to contribute less to the overall reaction because they burn slowly compared to the smaller particles.
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Journal: Combustion and Flame
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.combustflame.2019.04.030
Volume: 205 Issue: First Page #: 327
Date Submitted: 8/8/19 12:00AM Date Published: 4/12/19 5:00AM
Publication Location:
Article Title: A strategy for increasing the energy release rate of aluminum by replacing the alumina passivation shell with aluminum iodate hexahydrate (AIH)
Authors: Joseph Kalman, Dylan K. Smith, Kelsea K. Miller, Sanjoy K. Bhattacharia, Kenneth R. Bratton, Michelle
Keywords: spectroscopy, flame speed, AIH, aluminum, diffusion barrier, diffusion reactions
Abstract: This study explores the reactive nature of AIH and nAl by examining ignition and energy transfer of two different AIH + nAl formulations. The first is AIH synthesized on the surface of nAl particles to a concentration ratio of 80 wt% AIH to 20 wt% nAl. This composite particle lacks the Al 2 O 3 shell that inherently passivates nAl and replacing it with AIH, these particles will be referred to as Particle AIH + Al . In comparison, a discrete mixture of 80 wt% AIH powder combined with 20 wt% nAl powder is also examined and the mixture is referred to as Mix AIH + Al . Laser ignition studies show ignition and burn times are reduced for Particle AIH + Al compared to Mix AIH + Al , owing to the presence of the Al 2 O 3 diffusion barrier that inhibits ignition in the Mix AIH + Al . Also, flame speed measurements reveal that Particle AIH + Al propagate at 3062 m/s while the Mix AIH + Al at 1366 m/s.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Optics and Lasers in Engineering
Publication Identifier Type: Publication Identifier:
Volume: 124 Issue: First Page #: 105841
Date Submitted: 8/25/20 12:00AM Date Published: 6/1/20 5:00AM
Publication Location:
Article Title: A Closer Look at Determining Burning Rates with Imaging Diagnostics
Authors: K. Ryan Bratton, Connor Woodruff, Loudon L. Campbell, Ronald J. Heaps, Michelle L. Pantoya
Keywords: burning rate, flame speed, high brightness imaging, thermites, energetic reactions, laser illumination imaging
Abstract: Energetic composites such as pyrotechnics and thermites often produce high-brightness reactions such that measuring burning rate is challenging because of camera sensor saturation. The objective of this study was to compare burning rate measurements of reacting powders utilizing various filtration and illumination techniques. Experiments were designed using aluminum (Al) and molybdenum trioxide (MoO3) powder mixtures.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Powder Technology
Publication Identifier Type: Publication Identifier:
Volume: 374 Issue: First Page #: 33
Date Submitted: 8/25/20 12:00AM Date Published: 7/3/20 5:00AM
Publication Location:
Article Title: Aluminum Particle Reactivity as a Function of Alumina Shell Structure: Amorphous versus Crystalline
Authors: Renita Walzel, Michelle L. Pantoya
Keywords: Flame Speed, Melt Dispersion Mechanism, Thermites, Aluminum, Diffusion Reactions, Fluorination Reactions
Abstract: Exothermic interface reactions between fluorine-containing polymers and the alumina (Al2O3) shell surrounding aluminum (Al) fuel particles promotes Al reactivity. Recent work indicates that if the Al2O3 shell is transitioned from its original amorphous phase into a crystalline phase, the calorific output from the pre-ignition and main oxidation reactions both increase. But, how the increased energy released effects energy propagation has not been studied. The objective is to investigate reactivity as a function of the Al2O3 shell phase. Aluminum particles are thermally treated to transition the shell from amorphous to crystalline and each powder is combined with polytetrafluoroethylene (PTFE). Flame speed is measured for Al+PTFE for two Al particle sizes varying from micrometer to nanometer diameter and for both crystalline and amorphous Al2O3 shells.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Thermochimica Acta
Publication Identifier Type: Publication Identifier:
Volume: 690 Issue: First Page #: 178701
Date Submitted: 8/25/20 12:00AM Date Published: 6/1/20 5:00AM
Publication Location:
Article Title: Thermal analysis of an iodine rich binder for energetic material applications
Authors: I. Shancita, Connor Woodruff, Loudon Lee Campbell, Michelle L. Pantoya
Keywords: Biocidal Materials, Iodine Reaction, Aluminum Combustion, Thermites, Ignition
Abstract: Biological agent defeat formulations containing an iodinated binder would offer a unique solution for biocide release, as a secondary neutralization step post combustion, in the form of iodine. This study describes the synthesis and development of an iodinated agent defeat binder (C20H30N4O2I4), followed by reactive characterization when combined with a thermite mixture, for example Al + Fe2O3. Laser ignition studies were performed to evaluate ignition time and energy, as well as in-situ monitoring of the reaction using a high speed camera. The thermite mixtures with binder exhibited 37% reduction in ignition energy and 80% decreased ignition delay time compared to the control. Also, analysis of binder decomposition using XRD and TGA-EGA shows that the majority of iodine is released in the gas phase upon thermal decomposition. Results indicate that a formulation can be tailored from these mixtures to optimize for combustion properties and iodine release in agent defeat applications.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: RSC Advances
Publication Identifier Type: DOI Publication Identifier: 10.1039/D0RA02250K
Volume: 10 Issue: 24 First Page #: 14403
Date Submitted: 8/25/20 12:00AM Date Published: 3/30/20 5:00AM
Publication Location:
Article Title: Synthesis of metal iodates from an energetic salt
Authors: I. Shancita, Kelsea K. Miller, Preston D. Silverstein, Joseph Kalman, Michelle L. Pantoya
Keywords: Halogen, Aluminum, Oxidation, Thermal Analysis, DSC, TGA, Metal Oxides
Abstract: Metal iodates have been shown to be strong oxidizers when combined with aluminum fuel particles for energy generating applications. One method to produce metal iodates in situ is by using metal oxides and an energetic salt: aluminum iodate hexahydrate (Al(H2O)6(IO3)3(HIO3)2), which is called AIH. In this study, the thermal stability and reactivity of AIH with metal oxides commonly used in energetic formulations was investigated. Three metal oxides: bismuth(III) oxide (Bi2O3), copper(II) oxide (CuO), and iron(III) oxide (Fe2O3) were investigated because of their different oxygen release properties. Each metal oxide powder was combined with AIH powder.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Thermal Analysis and Calorimetry
Publication Identifier Type: DOI Publication Identifier: 10.1007/s10973-020-09742-4
Volume: Issue: First Page #:
Date Submitted: 8/25/20 12:00AM Date Published: 5/1/20 5:00AM
Publication Location:
Article Title: Thermal analysis of microscale aluminum particles coated with perfluorotetradecanoic (PFTD) acid
Authors: Loudon L. Campbell, Kevin J. Hill, Dylan K. Smith, Michelle L. Pantoya
Keywords: Fluoropolymers, Aluminum, IR Imaging, Surface Coatings, Powder, Flame Temperature
Abstract: One way to enhance Al particle reaction is to coat the particle surface with a condensed phase oxidizing agent that is in immediate contact with the particle surface to promote diffusion reactions. Fluorocarbons such as perfluorocarboxylic acids have been used to enhance Al combustion for nanoscale Al (nAl) particles because fluorinated species are also reactive with the Al2O3 passivation shell surrounding the Al core particle. This study extends previous work on nAl toward ?Al particles coated with perfluorotetradecanoic acid (PFTD) (F3C(CF2)11CO2H) and then characterizes the ?Al-PFTD thermal reactivity.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: MRS Advances
Publication Identifier Type: Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 8/25/20 12:00AM Date Published: 3/12/19 5:00AM
Publication Location:
Article Title: Material characterization of plasma-treated aluminum particles via different gases
Authors: C.-C. Wu, Kelsea K. Miller, Scott D. Walck, Michelle Pantoya
Keywords: Plasma Processing, Surface Chemistry, Powders, Surface Roughness, TEM
Abstract: This work describes exploration of mitigating the parasitic amorphous alumina (Al2O3) shell of aluminum nanoparticles (n-Al) and modifying the surface using different plasmas, leading to n-Al with thinner shell and different coatings including carbons and oxidizing salt called aluminum iodate hexahydrate (AIH), respectively. The approach exploits a prototype atmospheric non-thermal plasma reactor with dielectric barrier discharge (DBD) configuration for nanoparticle surface modifications using n-Al of 80 nm average diameter as an example. Preliminary results indicate that the amorphous Al2O3 shell surrounding the active aluminum core can be mitigated with inert plasmas by as much as 40% using either helium (He) or argon (Ar).
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Aerospace America
Publication Identifier Type: Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 8/25/20 12:00AM Date Published: 12/2/19 6:00AM
Publication Location:
Article Title: Innovations made on NASA initiator, 3D printing of propellants, cool gas generators
Authors: J. F. Zevenbergen
Keywords: Propulsion, Energy
Abstract: A Year-in-Review piece for AIAA.
Distribution Statement: 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Combustion and Flame
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.combustflame.2020.12.024
Volume: 226 Issue: First Page #: 419
Date Submitted: 8/25/21 12:00AM Date Published: 4/1/21 5:00AM
Publication Location:
Article Title: Regulating magnesium combustion using surface chemistry and heating rate
Authors: Islam Shancita, Neil G. Vaz, Guilherme D. Fernandes, Adelia J.A. Aquino, Daniel Tunega, Michelle L. P
Keywords: Magnesium, Magnesium Oxide, Magnesium Hydroxide, Magnesium Fluoride, Surface Chemistry, Perfluoropolymethyer
Abstract: The magnesium (Mg) particle surface can be used to regulate fluorination or oxidation reactions depending on the applied heating rate and Mg particle size. Magnesium particles are surrounded by a complex hydroxide shell composed of an inner layer of magnesium oxide (MgO) and outer layer of magnesium hydroxide (Mg(OH) 2). As particles approach the nanoscale, the thick oxide shell (e.g., 22 nm) becomes an appreciable portion of the overall powder and can be exploited to regulate reactivity. In this study, the reactivity of 800 nm Mg particles (nMg) was compared to 44 ?m Mg particles (?Mg) when combined with Perfluoropolyethyer (PFPE), providing both fluorine and oxygen for Mg reactions. Experiments were performed at slow heating rates (10 ° C/min) and separate experiments were performed at fast heating rates (6.0 ×10 5 °C/min).
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Applied Optics
Publication Identifier Type: DOI Publication Identifier: 10.1364/AO.423924
Volume: 60 Issue: 16 First Page #: 4976
Date Submitted: 8/25/21 12:00AM Date Published: 6/1/21 5:00AM
Publication Location:
Article Title: Comparison of pyrometry and thermography for thermal analysis of thermite reactions
Authors: Connor Woodruff, Steven W. Dean, Michelle L. Pantoya
Keywords: Aluminum Combustion, Reaction Temperatures, Infrared, Emissivity, Thermography, Pyrometry
Abstract: This study examines the thermal behavior of a laser ignited thermite composed of aluminum and bismuth trioxide. Temperature data were collected during the reaction using a four-color pyrometer and a high-speed color camera modified for thermography. The two diagnostics were arranged to collect data simultaneously, with similar fields of view and with similar data acquisition rates, so that the two techniques could be directly compared. Results showthat at initial and final stages of the reaction, a lower signal-to-noise ratio affects the accuracy of the measured temperatures. Both diagnostics captured the same trends in transient thermal behavior, but the average temperatures measured with thermography were about 750 K higher than those from the pyrometer. This difference was attributed to the lower dynamic range of the thermography camera's image sensor, which was unable to resolve cooler temperatures in the field of view as well as the photomultiplier tube sensors in the pyrometer.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/5.0040189
Volume: 154 Issue: 10 First Page #: 104308
Date Submitted: 8/25/21 12:00AM Date Published: 3/1/21 6:00AM
Publication Location:
Article Title: Reaction mechanism for fluorination reactions with hydroxylated alumina sites: Pathways promoting aluminum combustion
Authors: Daniel Tunega, Michelle L. Pantoya, Reed Nieman, Hans Lischka, Adelia J. A. Aquino
Keywords: Density Functional Theory, Molecular Dynamic Simulations, Fluorine, Aluminum Particle Combustion, Fluorinated Binders
Abstract: Density functional theory calculations were used to reveal the mechanism for the fluorination reaction of active Lewis acid sites on alumina structures, which is important in understanding the pyrophoric processes involving Al particles. In this reaction, hydroxyl groups of active sites are replaced by fluorine anions. Alumina structures were represented by three aluminum aqua hydroxo clusters (labeled AlOOH), in which the Al atom had different coordination spheres, particularly four, five, or six. The F-bearing molecules HF, CH3F, and CF4 were taken as reactants for the fluorination reactions. The overall reaction was represented by four reaction steps as follows: (i) formation of the reaction complex, (ii) activation of the transition state (TS), (iii) deactivation of the TS with a formation of the product complex, and (iv) its decomplexation to individual products.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 2-Awaiting Publicat
Journal: Journal of DoD Science & Engineering
Publication Identifier Type: Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 8/26/21 12:00AM Date Published:
Publication Location:
Article Title: Strategy for enhancing fast energy release from aluminum nanoparticles based on activation energy analysis
Authors: Sanjoy Bhattacharia, Kelsea Miller, Jennifer Gottfried, Michelle Pantoya
Keywords: aluminum combustion, ignition energy, reaction mechanism, iodine oxides
Abstract: Aluminum powder is used in military formulations to enhance late-time explosive effects due to its delayed reactivity. The popularity of energetics research involving nanoscale aluminum (nAl) particles stems from their higher specific surface area and thus faster reactivity with the potential to enhance microsecond-timescale detonation performance. However, the formation of an alumina (Al2O3) passivation layer serves as a barrier to rapid oxidation. Recent research demonstrated that an iodic acid solution modified the surface of nAl powder by forming a reactive crystalline layer of aluminum iodate hexahydrate (AIH) ([Al(H2O)6](IO3)(HIO3)2) that partially replaced the alumina passivation layer. The AIH-coated nAl particles (nAl@AIH) showed significantly faster microsecond-timescale energy release compared to unmodified nAl in lab-scale energetic testing based on laser-induced air shock from energetic materials (LASEM).
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Publication Type: Journal Article Peer Reviewed: N **Publication Status:** 1-Published
Journal: ARL-TR-9167
Publication Identifier Type: Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 8/26/21 12:00AM Date Published: 3/31/21 5:00AM
Publication Location:
Article Title: Plasma-Tailored Smart Surface Aluminum Nanoparticles
Authors: Chi-Chin Wu, Jennifer Gottfried, Kelsea Miller, Rose Pesce-Rodriguez, Scott Walck, Lily Giri, Jianguo W
Keywords: Surface Science, Powder Processing, Aluminum Combustion, Etching, Alumina
Abstract: This work describes the exploration of mitigating the parasitic amorphous alumina (Al2O3) shell of aluminum nanoparticles and modifying the surface using helium (He) and argon (Ar) plasmas in dielectric barrier discharge reactors, followed by mixing in acidic iodic solution to synthesize energetic Al coated with an effective oxidizer called aluminum iodate hexahydrate (AIH), that is, Al@AIH. Via either He or Ar plasma for 10 or 30 min; the oxide shell thickness was successfully reduced from 4–6 nm to an average 3 nm (40% reduction). The resultant plasma-treated Al@AIH exhibited significantly faster energy release rates at the microsecond timescale in comparison to conventional 6 wt% and 15 wt% Al@AIH samples and individual components associated with Al@AIH formation. Scanning transmission electron microscopy (STEM) elemental maps indicated a more uniform AIH distribution on He-plasma-treated Al than on the Ar-plasma-treated sample.
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Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: N **Publication Status:** 1-Published
Journal: ARL Technical Note 1072
Publication Identifier Type: Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 8/26/21 12:00AM Date Published: 8/1/21 5:00AM
Publication Location:
Article Title: High-Pressure Thermal and Aging Behavior of Aluminum Iodate Hexahydrate
Authors: RA Pesce-Rodriguez, JL Gottfried, L Giri, KK Miller, ML Pantoya
Keywords: Aluminum Combustion, Iodates, Energy Release Rates, Detonation Reactions, Equilibrium Kinetics
Abstract: Neat aluminum iodate hexahydrate (AIH) was characterized at high pressures and high heating rates to understand the apparent inconsistency between the high laser-induced shock velocities observed via laser-induced air shock from energetic materials (LASEM) and the endothermic behavior observed by conventional differential scanning calorimetry (DSC). Unlike conventional DSC, LASEM experimental conditions include high heating rates (~1013 K/s) and transient high pressures exceeding 10 GPa—and the LASEM results indicate exothermic energy release occurs on the microsecond timescale following laser excitation. Exothermic decomposition transitions of AIH were demonstrated for the first time when DSC was run under high pressure (up to 650 psi). Results for Flash DSC (at heating rates from 100 to 100,000 °C/s) show rapid heating rates alone are insufficient for manifesting exothermic behavior for AIH and suggest high pressure is required.
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CONFERENCE PAPERS:

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Optical Society of America (OSA)
Date Received: 30-Aug-2018 Conference Date: 18-Jun-2018 Date Published:
Conference Location: Orlando, FL
Paper Title: Measuring Flame Speeds with High Speed Imaging Diagnostics
Authors: Bratton, K. R., Woodruff, C. Campbell, L.L., Pantoya, M.L., Heaps, R. J.,
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: ACS Fluoropolymer 2018
Date Received: 30-Aug-2018 Conference Date: 20-Jun-2018 Date Published: 20-Jun-2018
Conference Location: Denver, CO USA
Paper Title: Piezoelectric Energetics: Synthesis and Reactivity of PVDF + Al Energetic Composites
Authors: 2. Sanjoy, B., Campbell, L.L., Ameduri, B., Pantoya, M.L.
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Gordon Research Conference on Energetic Materials
Date Received: 30-Aug-2018 Conference Date: 04-Jun-2018 Date Published: 04-Jun-2018
Conference Location: Newry, ME, USA
Paper Title: Formation Mechanism and Reactivity of Aluminum Iodate Hexahydrate Crystals on Al2O3 and AlO (OH) nanoparticles
Authors: Shancita, I., Bhattacharia, S.K., Pantoya, M.L., Wu, C.C.,
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Gordon Research Conference on Energetic Materials
Date Received: 30-Aug-2018 Conference Date: 04-Jun-2018 Date Published: 04-Jun-2018
Conference Location: Newry, ME, USA
Paper Title: Additive Manufacturing for Mock Energetics
Authors: Campbell, L.L., Pantoya, M.L.
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Gordon Research Conference on Energetic Materials
Date Received: 30-Aug-2018 Conference Date: 04-Jun-2018 Date Published: 04-Jun-2018
Conference Location: Newry, ME, USA
Paper Title: The influence of oxidizing salt on the reactivity of aluminum
Authors: Miller, K., Smith, D., Bhattacharia, S., Pantoya, M.L.
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Gordon Research Conference on Energetic Materials,
Date Received: 30-Aug-2018 Conference Date: 04-Jun-2018 Date Published: 04-Jun-2018
Conference Location: Newry, ME, USA
Paper Title: Origin of Very High Reactivity of Aluminum iodate hexahydrate (AIH)
Authors: Sanjoy, B., Smith, D., Pantoya, M.L.
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: Materials Research Society (MRS) Fall Meeting 2017 Symposium PM2: Advances and Upcoming Research Strategies in Reactive Materials
Date Received: 31-Aug-2018 Conference Date: 04-Dec-2017 Date Published: 04-Dec-2017
Conference Location: Boston, MA USA
Paper Title: Replacing the Alumina Shell on Aluminum Particles with and An Energetic Salt
Authors: M. L. Pantoya, D. Smith
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: American Physical Society (APS)
Date Received: 31-Aug-2018 Conference Date: 12-Mar-2018 Date Published: 12-Mar-2018
Conference Location: Los Angeles, CA USA
Paper Title: Structural investigation of aluminum nanoparticles as energetic materials
Authors: Chi-Chin Wu, Dylan Smith, Michelle L. Pantoya
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 0-Other
Conference Name: ARDEC Picatinny Arsenal Invited Seminar
Date Received: 31-Aug-2018 Conference Date: 16-Nov-2017 Date Published: 16-Nov-2017
Conference Location: Picatinny, NJ USA
Paper Title: Three Dimensional Architectures of a Mock Energetic Material Using a Modified Fused Deposition Model Printer
Authors: Loudon (Lee) Campbell, Michelle L. Pantoya
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: North American Thermal Analysis Society (NATAS)
Date Received: 31-Aug-2018 Conference Date: 07-Aug-2018 Date Published:
Conference Location: Pennsylvania, USA
Paper Title: Origin of Very High Reactivity of Aluminum Iodate Hexahydrate (AIH)
Authors: S.K. Bhattacharia, D. Smith, K. Miller, M.L. Pantoya
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 3-Accepted
Conference Name: 66th JANNAF Propulsion
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I certify that the information in the report is complete and accurate:
Signature: Michelle Pantoya
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Project Summary - Grant # W911NF-17-1-0387
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Surface Chemistry Promoting Energetic Material Combustion

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Objective

This project examines surface reactions of aluminum particles with various halogen containing oxidizers (i.e., fluorine and iodine) as well as ignition and combustion properties affected by these surface reactions. The main goal is to enhance aluminum reactivity through understanding surface exothermic kinetics that facilitate combustion. The surface reactions are triggered by a halogen species, such as in fluoropolymers or in iodine or chlorine molecules. The objective is to understand the reaction kinetics of halogens with the alumina passivation shell surrounding aluminum particles, then use this understanding to design formulations that show greater reactivity. Our focus is on three areas of research including: (1) developing mechanistic understanding of reaction pathways that promote surface reactions; (2) analyzing and modeling Al combustion for ignition and energy propagation; and, (3) synthesizing and characterizing novel formulations that capitalize on the surface reactions.

Specific research questions: (1) How does surface chemistry affect oxidation, chemical energy generation, and energy release rates; (2) What reaction pathways are needed to promote the surface reactions; (3) How can the alumina surface be manipulated to enhance surface reactions; (4) What reaction kinetics accelerate oxidation rates and how can those kinetics be exploited to synthesize new formulations; (5) What controlling mechanisms and modes of energy transport are dominant and how do those mechanisms vary with oxidizer.

Approach

- Analyze the surface chemistry and reaction kinetics of metal – halogen formulations. Understand key chemical interactions between Al fuel (including passivation shell) and halogen species that lead to energy buildup, ignition, and accelerated reaction kinetics. Correlate these findings to macroscopic energy release rates and identify reaction mechanisms.
- Synthesize Al formulations that exploit alumina surface reactions and enable investigation of tailored parameters. Characterize these novel materials for their microscopic and macroscopic properties and analyze their influence on reactivity.

Relevance to Army – This research will:

- Analyze the physics and chemistry of energy buildup in aluminum that translates to greater reactivity in field applications and provides the Army with capability to reduce the weight of ordnance or re-design field systems for mission specific applications.
- Produce safer formulations with tailored performance. Ignition sensitivity can be tailored as well as energy generation rates and more complete conversion. Shelf-life (e.g., aging) will be improved and overall metal fuel performance increased.
- Understand surface reaction chemistry between fuel surfaces and halogen-containing, binder-based materials that will promote development of primers and other igniters, thin film power generation systems, and applications requiring detection of energetic materials.

- Improve aluminum combustion that will translate to new, greener energetic materials with enhanced performance and safety and adaptable initiation. This is critical for improving efficiency of warheads, gun/missile propellants, and insensitive munitions.
- Gain knowledge on enhanced combustion performance based on surface chemistry of aluminum particles that will transfer to other fuel particles such as magnesium, boron, and silicon. The fundamental research developed here will extend to enhancing performance of other metal fuels.
- Develop methodologies for experimental testing that will be valuable for studies of reactive processes in combustion, catalysis, fuel cells, and other civilian applications.
- Develop fundamentals for additive manufacturing (3D printing) for energetic materials. All 3D printing techniques require the integration of a polymer based oxidizer (binder). This work will enable knowledgeable selection of binder for tailored reaction with aluminum.

Accomplishments for Reporting Period

We are identifying key reaction pathways that promote surface chemistry and enhance overall Al reactivity. To harness greater power from Al combustion one approach is to chemically transform the Al_2O_3 passivation layer surrounding the Al core particle by exploiting surface reactions via wet chemistry. A goal was to identify key parameters affecting interfacial chemistry on Al particles specific to the formation of aluminum iodate hexahydrate (AIH). Experiments were designed using a range of diagnostics including XRD, XPS, TEM, DSC, TGA, LASEM, and more. Results showed *AIH formation is facilitated on hydrated alumina surfaces* and specifically, AIH formation is linked to removal of terminal OH bonds **[1]**. In fact, a systematic approach was designed to synthesize pure AIH from $Al(OH)_3$ powder that was immersed in iodic acid solution. **Figure 1** shows an SEM image of pure AIH crystals along with the X-ray diffraction pattern [**2**]. The AIH crystals are highly reactive as an oxidizer when combined with metal fuel particles. In fact, **Fig. 2** shows flame speeds measured for mixtures of AIH and Al compared with AIH that is coated on Al particles [**2**]. As a coating, the AIH has no significant barrier such that diffusion reactions are accelerated and the flame speeds correspondingly increase. This understanding informs new synthesis strategies that are tailored to preparing Al particles with purposefully hydrated surface coatings (see **Fig. 3** concept sketch). The hydration layer will be used in future work to catalyze specific reactions that will transform the aluminum particle's shell chemistry toward altered (enhanced) reactivity.

We explored alternative methods for altering the shell chemistry that included mitigating the Al_2O_3 shell using different gas discharge plasmas leading to Al particles with a thinner shell. This work was done by Ms. Kelsea Miller (TTU) at Aberdeen Proving Ground (APG) using Dr. Chi-Chin Wu's dielectric barrier discharge (DBD) plasma apparatus (see **Fig. 4**). Two gas discharge plasmas were examined: helium (He) and argon (Ar), and both induced thinning of the Al shell (**Fig. 5**) [**3**]. Interestingly, the Ar plasma promoted significant hydration of the Al particle surface. **Fig. 6** shows TGA data that revealed significant mass loss associated with the hydrated Ar plasma treated Al particles and XRD data analysis with Rietveld Refinement indicated about 50% of the Ar plasma treated particles became a hydrated form of alumina, specifically boehmite: AlO(OH). This form of hydrated alumina is actually the most stable and does not readily transform into AIH.

All plasma treated Al particles were then further processed in an iodic acid solution. The results showed all the plasma treated Al particles produced many iodine-containing species on the surface, including: HIO_3, HI_3O_8, and AIH [**3**]. **Figure 7** shows TEM images of the Al particle surfaces decorated with iodine-species and **Fig. 8** shows the concentration of different iodine species detected via XRD data analysis using Rietveld Refinement. **Figures 7 and 8** reveal two very interesting features: (1) When Al particles are plasma treated to induce shell thinning, what is likely happening is the outer hydration layer is reduced. With the reduction of a hydration layer when the particles are immersed in iodic acid, the iodine species that form are more localized on the surface. Specifically, the iodine species decorate the particles as opposed to fully coat the particle as seen for non-plasma treated Al particles (**Fig.7**) [**3**]. (2) For the wet-chemistry conditions studied here, the iodine species decorating plasma treated Al particles have various chemistries (i.e., HIO_3, HI_3O_8, and AIH) whereas when non-plasma treated Al particles were immersed in iodic acid, 100% of the transformation is to AIH. The differences in chemical composition of surface species may be attributed to the wet chemistry conditions. Specifically, the plasma treated particles were not immersed in the iodic acid long enough to allow complete transformation to AIH. Energetic tests utilizing laser-induced air shock for energetic materials (LASEM) show significantly enhanced energy release rates at the µs timescale for plasma treated nAl decorated with iodine species (**Fig. 9**). The LASEM tests indicate that there is great potential for using this methodology to prepare Al particles for further chemical treatment and show that chemical treatment of Al particles significantly impacts their reactivity at time scales relevant to a detonation event.

In another study, we used pure AIH synthesized in our lab (see **Fig. 1**) in reactions with metal oxides [**4**]. This study showed that AIH reacts with metal oxides exothermically to form metal iodates, *in-situ* of the reaction. The significance of this understanding is that upon AIH decomposition, metal iodates are actually more stable than the metal oxides and metal iodates are good oxidizers for fuel particle reactions. So, by forming metal iodiates *in-situ* a reaction, AIH contributes towards increasing the reaction pathways for Al combustion in a mixture with CuO (e.g., Al + AIH, Al + CuO, Al + $CuIO_3$). Also, the formation of metal iodates is exothermic such that the AIH + Metal Oxide reactions actually contribute exothermic energy to the overall reactivity. Further tests are on-going to understand these ternary reactions.

We have started to extend our research on surface chemistry to other fuel particles. Specifically, we started studying magnesium (Mg) particles because of its similar properties compared to Al (e.g., similar core-shell structure, similar melting temperatures of core and shell, similar core-shell strength properties). Magnesium particles are surrounded by a complex hydroxide shell composed of an inner layer of magnesium oxide (MgO) and outer layer of magnesium hydroxide ($Mg(OH)_2$). This hydrated structure shows promise for surface chemistry alterations of Mg, but we started with a more basic analysis of surface chemistry that is a function of particle size. As Mg particles approach the nanoscale, the thick oxide shell (e.g., 22 nm) becomes an appreciable portion of the overall powder. In this study [**5**], the reactivity of 800 nm Mg particles (nMg) was compared to 44 µm Mg particles (µMg) when combined with Perfluoropolyethyer (PFPE), providing both fluorine and oxygen for Mg reactions. Experiments were performed at slow heating rates (10°C/min) and separate experiments were performed at fast heating rates (6.0×10^5 °C/min). For nMg powders, the outer $Mg(OH)_2$ surface layer dehydrates at low temperatures (313°C) creating highly reactive sites for surface oxidation reactions in the condensed phase leading to a higher conversion of $Mg(OH)_2$ to MgO and greater consumption of Mg through oxidation reactions. For µMg, higher $Mg(OH)_2$ dehydration temperatures (498°C) stabilize µMg particles and the bulk of reactions occur at elevated temperatures and in the gas phase producing higher MgF_2 concentrations. Under high heating rate conditions, MgF_2 formation is favored over MgO formation for both particle sizes owing to the high reaction temperatures that promote gas phase reactions. The results from this study are summarized in a single graphic (**Fig. 11**) and suggest that surface chemistry induced by an iodic acid solution will be a strong function of the particle size, and could significantly affect the smaller, nanoscale particles owing to the higher contribution of $Mg(OH)_2$. The next step in this work is to use pure $Mg(OH)_2$ particles in iodic acid solution to synthesize a magnesium-iodate-hydrate crystal structure.

Collaborations and Technology Transfer

- Drs. Brian Fuchs (**ARL, ARDEC, Picatinny Arsenal**), Andrew Ihnen (NAWC-WD), Didier Montaigne (AFRL, Eglin AFB) – We are leveraging our ARO project on Al fuel particles with on-going additive manufacturing development at Picatinny Arsenal. *Mr. Loudon Lee Campbell* is the TTU student working on this project that includes the design of a variable density printing system. The goal of the printing system is to process energetic formulations into tailored architectures with density gradients. Mr. Campbell's dissertation will be focused on the design and development of the 3D printing system.

- Drs. Chi-Chin Wu, Jennifer Gottfried, Rose Pecase-Rodrigez, Scott Walck, Kevin McNesby (**ARL, APG**) – We have been collaborating with Dr. Wu on plasma surface treatment of Al particles. Dr. Chi-Chin was awarded an ARL external collaboration initiative (ECI) to help support further plasma surface treatment studies on fuel particles. *Ms. Kelsea Miller* is the TTU student working on this project and has worked at APG in the summer of 2018 & 2019. She processed the plasma treated Al particles in iodic acids to develop an AIH surface coating and Dr. Gottfried studied these samples using LASEM. Scott Walck has been working with us on TEM analysis of surface and interface properties of aluminum particles. Dr. McNesby donated a high speed camera filter that will enable us to more accurately resolve high temperatures from data collected using our Phantom high speed color camera.
- Dr. Dylan Smith (**Eglin AFB**) –continues to engage in helpful discussions with us promoting our understanding of AIH formation.
- Dr. Robert Carl Brothers (**NSWC-IHEODTD**) –is a synthetic chemist that has been developing iodine-fluorine containing binders. He has shared some of his materials with us and we are studying the reactive behaviors with aluminum.

Resulting Journal Publications During Reporting Period

1. Shancita, I., Campbell, L.L., Wu, C.C., Walck, S.D., Aquino, A., Tunega, D., Pantoya, M.L., The effect of hydration on promoting oxidative reactions with aluminum oxide and oxyhydroxide nanoparticles, *J of Phys Chem C* 123, 15017-15026, 2019.
2. Kalman, J., Smith, D.K., Miller, K.K., Bratton, K.R., Pantoya, M.L., A strategy for increasing the energy release rate of aluminum by replacing the alumina passivation shell with aluminum iodate hexahydrate (AIH), *Comb Flame* **205**, 327-335, 2019.
3. Miller, K., Shancita, I., Bhattacharia, S., Pantoya, M.L., Atmospheric Pressure Plasma Surface Treatment on Aluminum Particles and Surface Reactions Altering the Alumina Shell Chemistry, Submitted to *J of Phys Chem C*, August 2020.
4. Shancita, I., Miller, K. K., Silverstein, P.D., Kalman, J., Pantoya, M.L., Synthesis of Metal Iodates from Aluminum Iodate Hexahydrate Salt, *RSC Advances* **10**, 14403-14409, 2020.
5. Shancita, I., Vaz, N., Fernandes, G., Aquino, A., Tunega, D., Pantoya, M.L., Regulating Magnesium Combustion Using Surface Chemistry and Heating Rate, Submitted to *J of Phys Chem C*, August 2020.
6. Bratton, K.R., Woodruff, C., Campbell, L.L., Heaps, R.J., Pantoya, M.L., A Closer Look at Determining Flame Speeds with Imaging Diagnostics, *Optics and Lasers in Engineering* 124, 105841, 2020.
7. Campbell, L.L., Hill, K. J., Smith, D.K., Pantoya, M.L., Thermal Analysis of Microscale Aluminum Particles Coated with Perfluorotetradecanoic (PFTD), *J Thermal Anal and Calorimetry*, 2020.
8. Shancita, I., Woodruff, C., Campbell, L.L., Pantoya, M.L., An Iodine Rich Binder for Energetic Material Applications, *Therm Acta,* 2020.
9. Walzel, R. K., Levitas, V.I., Pantoya, M.L., Aluminum particle reactivity as a function of the alumina shell structure: amorphous versus crystalline, *Powder Technology*, 374, 33-39, 2020.

Graduate Students Involved During Reporting Period

- Kelsea Miller (PhD)
- Shancita Islam (PhD)
- Ryan Bratton (PhD)
- Loudon (Lee) Campbell (PhD)
- Colt Cagle (BS, MS, PhD)
- Renita Walzel (MS)
- Connor Woodruff (PhD)
- Luke Croessmann (BS, PhD)

Awards, Honors and Appointments

M. Pantoya received a TTU Outstanding Research Award in May, 2020. K. Miller (PhD) and Luke Croessmann (PhD) was appointed at *Aberdeen Proving Ground* as a Summer Intern; L. Campbell (PhD) was appointed at *Picatinny Arsenal ARDEC* as an Engineering Intern (2020).

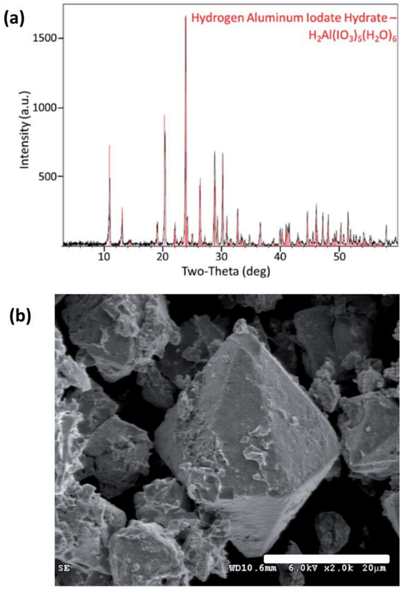


Figure 1. (a) Diffraction pattern from PXRD measurement indicating pure AIH powder (the red lines indicate the AIH reference overlaps the measured peaks). Data was collected from 0–90° 2θ with parallel beam geometry in continuous θ –2 θ mode with a collection time of 2° min^{-1} and a step size of 0.02°. (b) SEM image depicting hexagonal pyramidal geometries of pure AIH crystals. Note 20 mm scale bar for reference. Image was taken with a Hitachi S-4300 high resolution field emission SEM at an accelerating voltage of 6 kV.

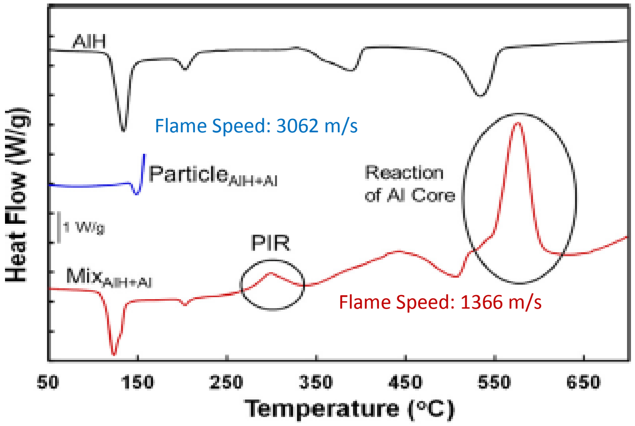


Figure 2. Heat flow as a function of temperature for a heating rate of 10 degrees per minute in an argon environment for pure AIH, a mixture of AIH and Al particles (Mix AIH+Al) and Al particles coated with AIH passivation shell (Particle AIH+Al). Flame speeds for respective mixtures are shown.

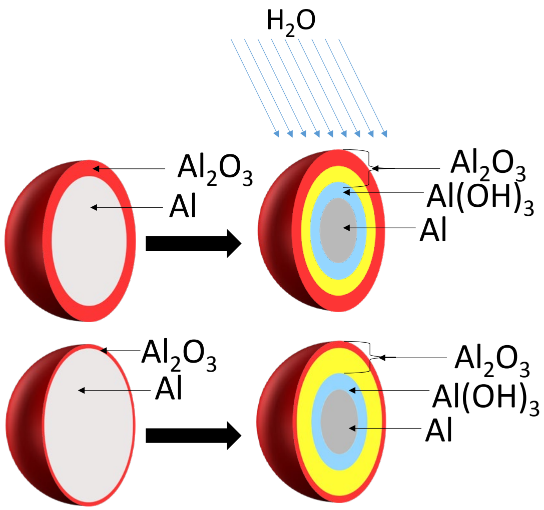


Figure 3. Schematic of an Al particle with two different shell thickness that could produce varied hydration structures upon H_2O dissociation induced surface reactions.

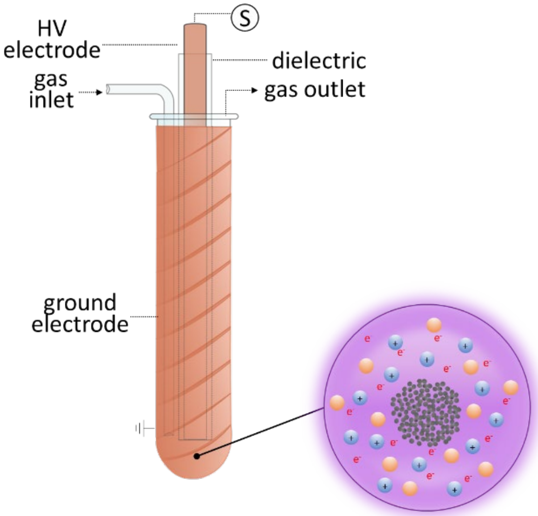
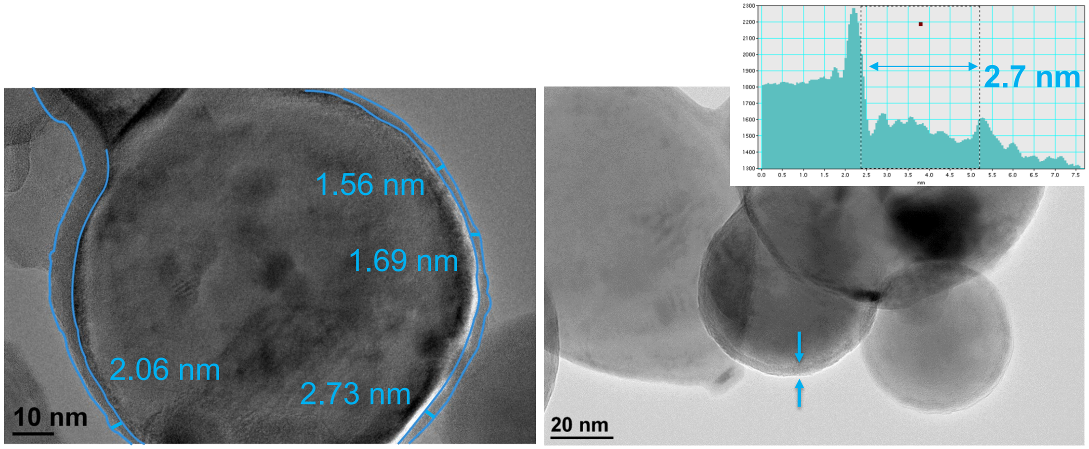


Figure 4. Schematic and photo of the DBD atmospheric plasma reactor setup.



10-min He plasma treatment **10-min Ar plasma treatment***

Figure 5. TEM images of plasma treated particles after exposure to two different plasma gas discharges: He and Ar. In both cases, the Al_2O_3 shell was thinned compared to the original thickness of the shell 3-5 nm.

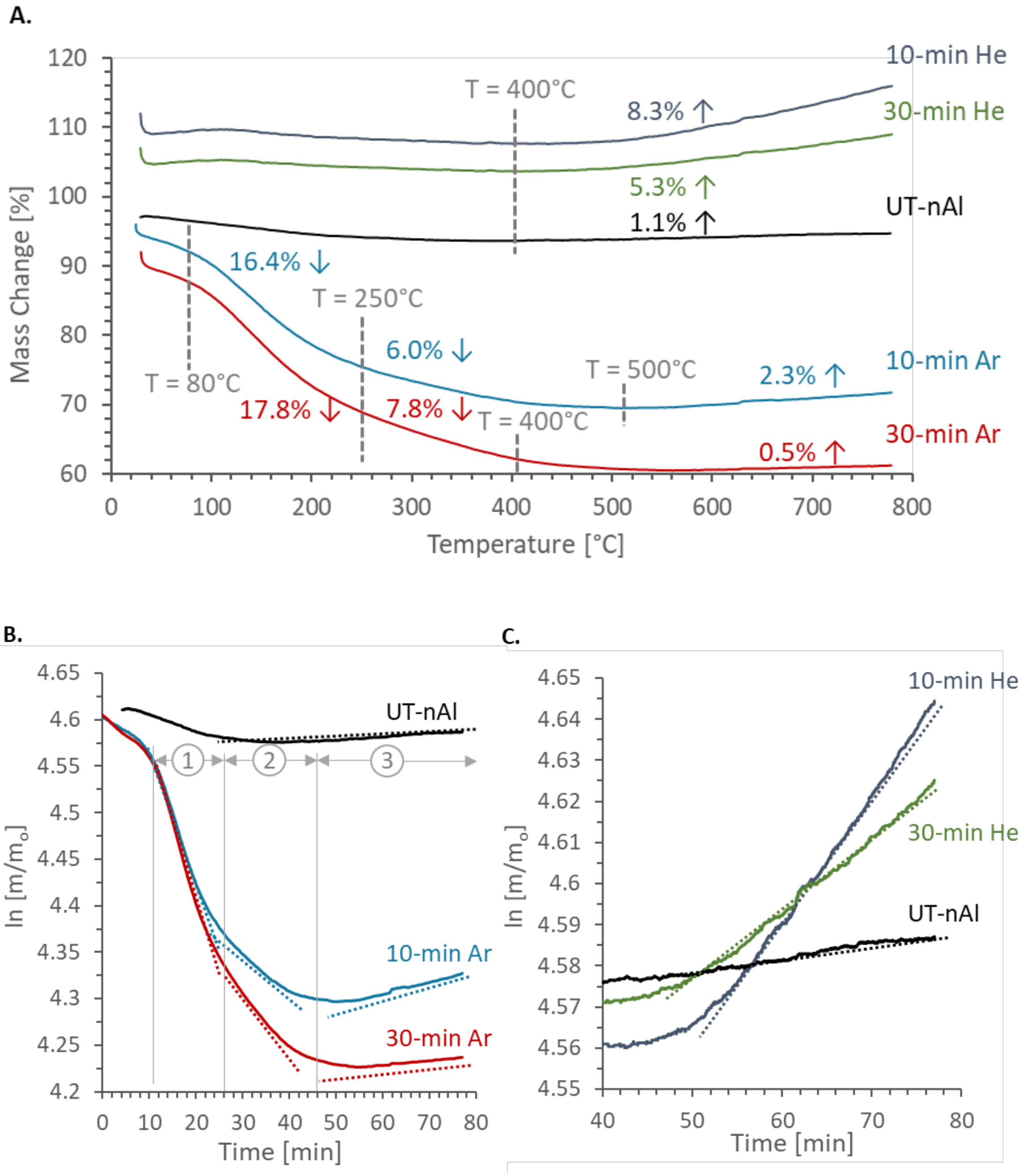


Figure 6. **A.** Mass changes of He-PT-nAl, Ar-PT-nAl and UT-nAl with ↑ representing mass gain and ↓ representing mass loss. **B.** Kinetic analysis for calculating the reaction rate constant, *k*, for Ar-PT-nAl and UT-nAl with dashed lines representing the rate of reaction occurring in each stage of decomposition. **C.** Kinetic analysis for calculating reaction rate constants for He-PT-nAl and UT-nAl with dashed lines representing the rate of oxidation occurring.

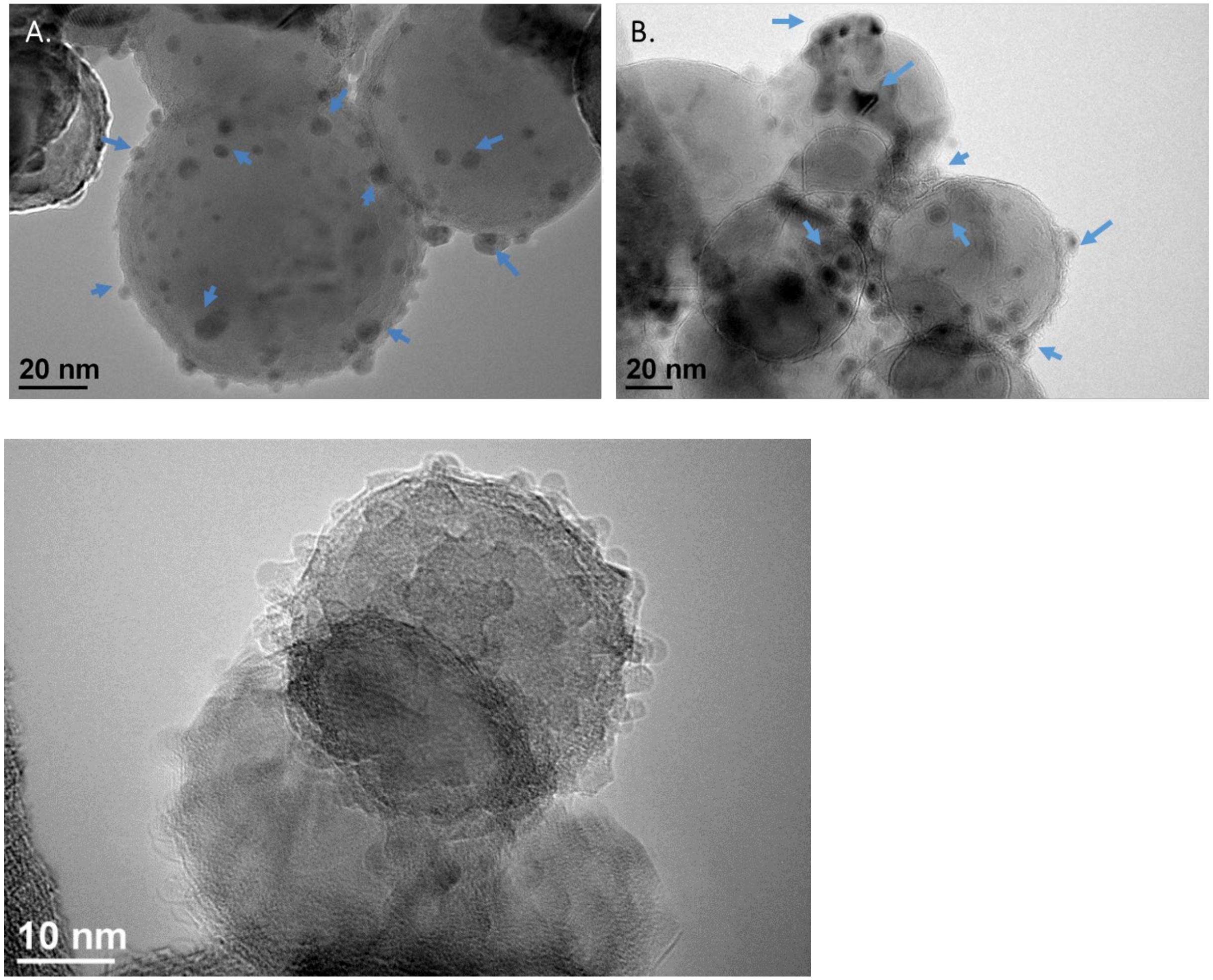


Figure 7. TEM BF images of 10-min (**A**) He PT-nAl-AIH and (**B**) Ar PT-nAl-AIH. (**C**) TEM image of an untreated, commercial Al particle that was immersed in iodic acid solution. The rough surface shows AIH coating surrounding the particle.

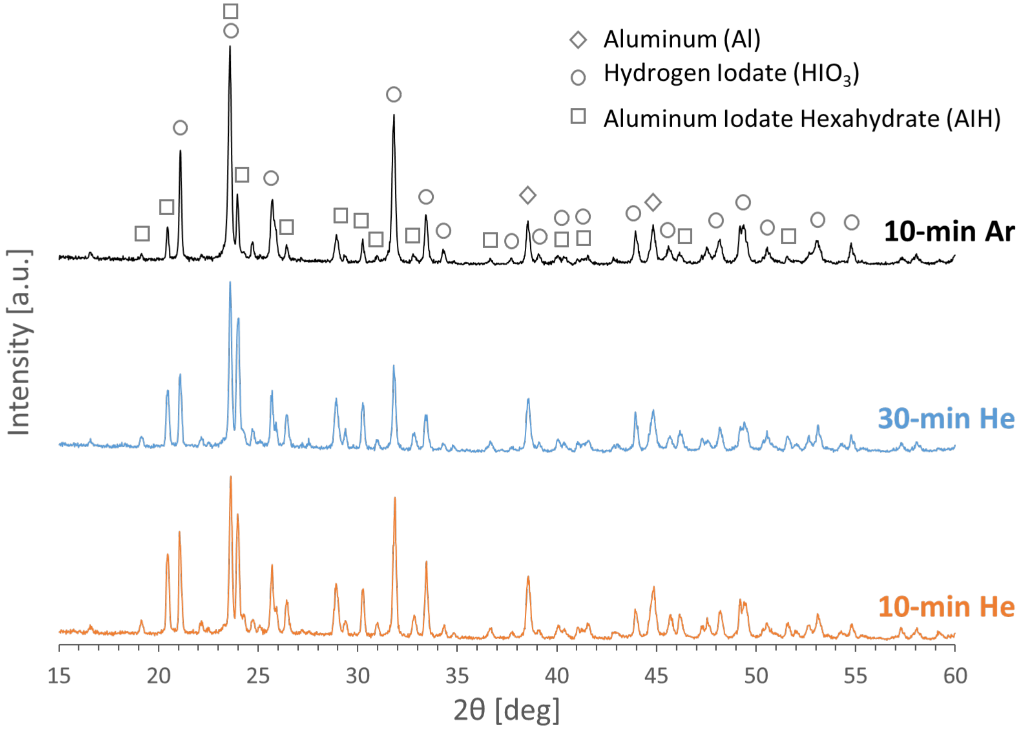


Figure 8. Powder XRD patterns of PT-nAl-AIH with identified crystalline species. **Table 5.** Crystalline species and amorphous content in PT-nAl-AIH powders from XRD data (**Fig. 8**) analysis using Rietveld refinement least squares curve fitting MDI Jade v9.1.1 software shown in *Supplementary Information.*

PT-nAl-AIH	AIH wt.% (σ)	Al wt.% (σ)	HIO_3 wt.% (σ)
10 min He	26.8 (0.6)	26.8 (1.5)	46.4 (1.0)
30 min He	33.7 (0.6)	28.6 (1.6)	37.7 (0.6)
10 min Ar	14.7 (0.4)	28.1 (1.6)	57.3 (1.2)

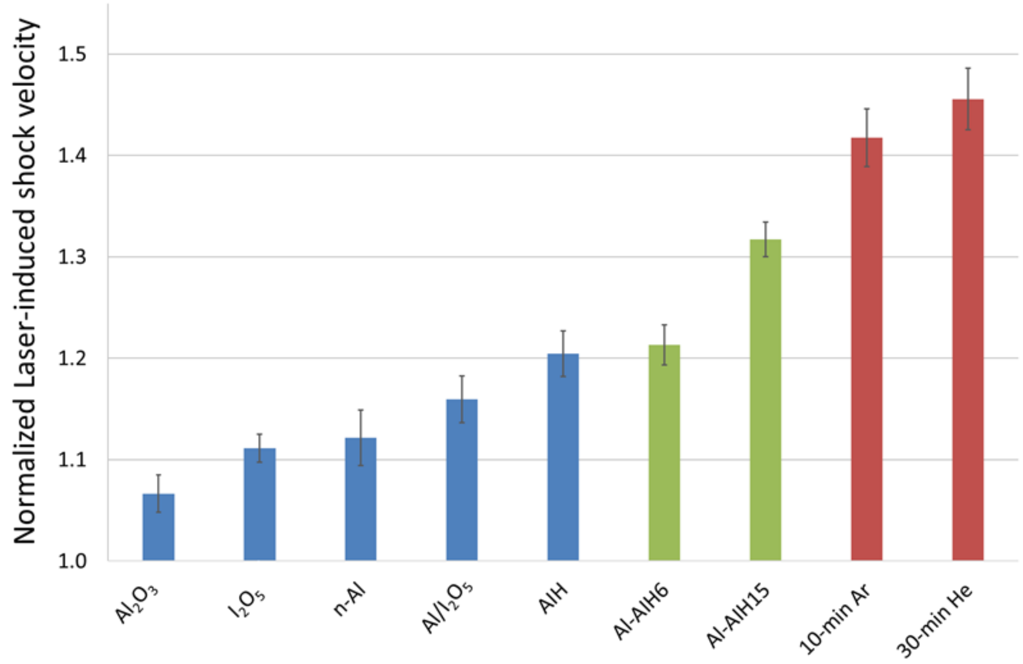


Figure 9. Laser induced air shock of energetic materials measurement of plasma treated Al samples with iodates decorated on the particles (red bars) compared to the building blocks of these materials (blue bars) and compared to Al particles coated with AIH at 6 and 15 %, respectively (green bars). The data is normalized against the tape used on the ablation experiments.

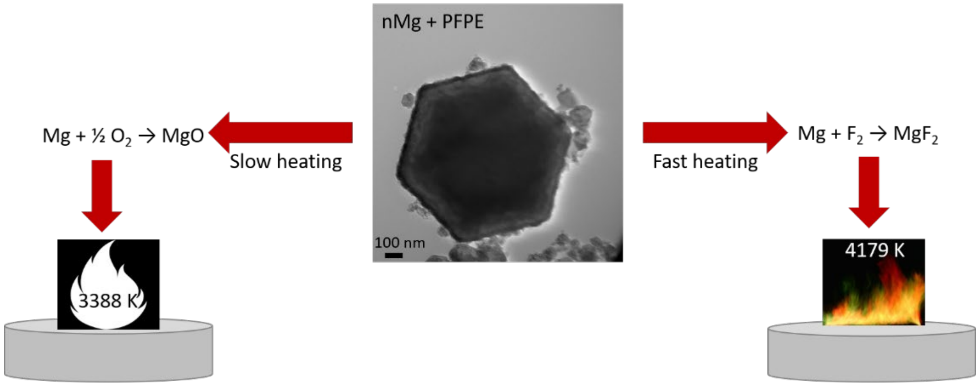


Figure 10. TEM image of a magnesium particle on the nanoscale. Under slow heating the dehydration of the passivation shell plays a dominant role in forming MgO whereas for faster heating fluorinated species from PFPE more favorably form MgF_2 product species. Results indicate nanoscale particles with significant hydration may be ideal of surface catalytic processes that promote new core-shell fuels with enhanced reactivity.