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# RPPR Final Report
as of 05-Mar-2019

Agency Code:

Proposal Number: 63153EG **Agreement Number: W911NF-13-1-0234**

**INVESTIGATOR(S):**

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**Principal:** Y

Organization: **University of Maryland - College Park**
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Phone: (301) 405-4311
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**STEM Degrees:** 3 **STEM Participants:** 5

**Major Goals:** Objective: The focus of this proposal is to understand quantitatively, the nature of the reactivity of nanoparticles and nanocomposites for energetic materials applications.

The proposal focuses on two major points.

Point 1: What physical–chemical properties make for a good oxidizer and why ? This implies we first need to get a better understanding of how an oxidizer functions in a reactive material.
Point 2: Why does the scaling law for the size dependence on burning rate decrease below unity, and what does this tell us about how to formulate a nano material?

Approach
We will employ a range of diagnostic tools and model materials to evaluate and refine our ideas and tweeze out both qualitative mechanistic information as well as quantitative kinetic information. We will use a combination of unique capabilities at the University of Maryland as well as a recent collaboration with LLNL.

The diagnostic tools to be employed include high resolution and high heating rate electron microscopes designed to evaluate the surface area of nanoscale materials relative to reaction times. T-Jump TOF mass spectrometry to evaluate metal oxide oxygen release kinetics and thermite reaction speciation. TGA-DSC measurements to evaluate reduction kinetics and melting transitions.

In order to correlate the importance of gas phase oxygen release vs. condensed phase oxygen ion-transport (within metal oxide) we will focus on prototype material systems (e.g. Perovskites and others) for which significant experimental and theoretical data already exists on oxygen ion-mobility. These materials can be produced in significant quantities using our Spray Pyrolysis capabilities with high control of stiochiometry.

The result of this project should answer some basic questions:
a. Does the fraction power law burning behavior related to loss of surface area.
b. What is the role of oxygen ion transport within the metal oxide in determining ignition and subsequent combustion behavior.

The answer to these question will enable a more scientific approach to choose fuel-oxidizer combinations as well as how to eventually assemble them to extract the highest thermodynamic potential, with the highest kinetic rate these materials can theoretically yield.

Relevance to Army: Energetic materials assembled at the Nanoscale offer the potential to yield more energy over shorter time frame, and thus more power. However critical questions remain as to the actual gains in the temporal energy profile. Furthermore to design materials with enhanced properties a better scientific understanding is needed. The focus is to provide DOD with the critical information needed to assess the utility of nanoenergetic materials to real world application. We will provide DOD with methods for characterizing the reaction kinetics on well controlled and understood reactive metal, oxidizers and their composites.

**Accomplishments:** See attached

**Training Opportunities:** Two PhD students were trained, plus a number of undergraduates.

**Results Dissemination:** - 41 referred publications
- conference proceedings
- Multiple conference talks and invited talks.

**Honors and Awards:** Nothing to Report

**Protocol Activity Status:**

**Technology Transfer:** - Collaboration with Greg Young, NSWC-IH
- Collaboration with B. Rice, ARL
- Collaboration with C. Johnson, NSWC-China Lake
- NiruTraveti, ARL

**PARTICIPANTS:**

**Participant Type:** Graduate Student (research assistant)
**Participant:** Xizheng Wang
**Person Months Worked:** 12.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
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Other Collaborators:

**Participant Type:** Graduate Student (research assistant)
**Participant:** Rohit Jacob
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International Travel:
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Other Collaborators:

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**Journal:** Journal of Propulsion and Power
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Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** The Effects of Aluminum Hydride as a Fuel Supplement on the Performance of Traditional NanoThermites
**Authors:**
**Keywords:** Energetics
**Abstract:** An experimental study was conducted in which aluminum hydride (alane, $AlH_3$) replaced nanoaluminum incrementally as a fuel in a nanocomposite thermite based on CuO, $Bi_2O_3$, and $Fe_2O_3$. Pressure cell and burn tube experiments demonstrated enhancements in absolute pressure, pressurization rate, and burning velocity when micron-scale aluminum hydride was used as a minor fuel component in a nanoaluminum–copper-oxide thermite mixture. Peak pressurization rates were found when the aluminum hydride made up about 25% of the fuel by mole. Pressurization rates increase by a factor of about two with the addition of $AlH_3$, whereas burn tube velocities increase by about 25%. The enhancement in pressurization rate appears to primarily be a result of the increased pressure associated with the $AlH_3$ decomposition in the nanocomposite thermite system and an enhancement in convective heat transfer. Similar experiments were conducted with micron-scale aluminum in place of the aluminum hydride, which resulted
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Publication Identifier Type: DOI Publication Identifier: 10.1016/j.combustflame.2013.10.017
Volume: 161 Issue: 5 First Page #: 0
Date Submitted: Date Published:
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**Article Title:** Do nanoenergetic particles remain nano-sized during combustion?
**Authors:**
**Keywords:** Energetics
**Abstract:** It is axiomatic that the burning time dependence on particle size follows an integer power law dependence. However, a considerable body of experimental data show a power dependence less than unity. In this paper, we focus on what might be responsible for the fractional power dependence observed for the burning time for nanoparticles (e.g. Al and B). Specifically we employ reactive molecular dynamics simulations of oxide-coated aluminum nanoparticles (Al-NPs). Since most nanomaterials experimentally investigated are aggregates, we study the behavior of the simplest aggregate – a doublet of two spheres. The thermo-mechanical response of an oxide coated Al-NP is found to be very different than its solid alumina counterpart, and in particular we find that the penetration of the core aluminum cations into the shell significantly softens it, resulting in sintering well below the melting point of pure alumina. For such coated nanoparticles, we find a strong induced electric field exists at th
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Publication Identifier Type: DOI Publication Identifier: 10.7567/JJAP.53.05HA10
Volume: 53 Issue: 0 First Page #: 0
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Publication Location:
**Article Title:** Nanosecond laser induced energetic ion formation from a nanoparticle: The origin of ion detection loss in a single particle mass spectrometry
**Authors:**
**Keywords:** laser initiations
**Abstract:** Here we study the interaction of a nanosecond laser pulse with a nanoparticle to explore the mechanism of energetic ion formation and in particular the particle size dependence. Multiphoton ionization and the subsequent electron impact ionization accompanied by inverse Bremsstrahlung process are determined appropriate for generation of multiple charged ions. The Coulomb expansion of a positive ion cloud is then calculated with molecular dynamics simulations, resulting in temporal evolution of ions, a radial distribution of kinetic energy of ions, and size-dependency of the ion kinetic energy. A mass spectrum peak of ion simulated by the present model is found comparable to the experimental data. Alternatively, a direct measurement of kinetic energy is also explained by the model.
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**Journal:** Journal of Applied Physics
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Volume: 115 Issue: 8 First Page #: 0
Date Submitted: Date Published:
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**Article Title:** In situ imaging of ultra-fast loss of nanostructure in nanoparticle aggregates
**Authors:**
**Keywords:** energetics
**Abstract:** The word “nanoparticle” nominally elicits a vision of an isolated sphere; however, the vast bulk of nanoparticulate material exists in an aggregated state. This can have significant implications for applications such as combustion, catalysis, and optical excitation, where particles are exposed to high temperature and rapid heating conditions. In such environments, particles become susceptible to morphological changes which can reduce surface area, often to the detriment of functionality. Here, we report on thermally-induced coalescence which can occur in aluminum nanoparticle aggregates subjected to rapid heating (106–1011 K/s). Using dynamic transmission electron microscopy, we observed morphological changes in nanoparticle aggregates occurring in as little as a few nanoseconds after the onset of heating. The time-resolved probes reveal that the morphological changes initiate within 15 ns and are completed in less than 50 ns. The morphological changes were found to have a threshold te
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Volume: 15 Issue: 8 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** Low Effective Activation Energies for Oxygen Release from Metal Oxides: Evidence for Mass-Transfer Limits at High Heating Rates
**Authors:**
**Keywords:** energetics
**Abstract:** Oxygen release from metal oxides at high temperatures is relevant to many thermally activated chemical processes, including chemical-looping combustion, solar thermochemical cycles and energetic thermite reactions. In this study, we evaluated the thermal decomposition of nanosized metal oxides under rapid heating (~105 Ks┐1) with time-resolved mass spectrometry. We found that the effective activation-energy values that were obtained using the Flynn–Wall–Ozawa isoconversional method are much lower than the values found at low heating rates, indicating that oxygen transport might be rate-determining at a high heating rate.
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Publication Identifier Type: DOI Publication Identifier: 10.1016/j.combustflame.2014.02.003
Volume: 161 Issue: 8 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** Assembly and reactive properties of Al/CuO based nanothermite microparticles
**Authors:**
**Keywords:** energetics
**Abstract:** It is generally agreed that a key parameter to high reactivity in nanothermites is intimate interfacial contact between fuel and oxidizer. Various approaches have been employed to combine fuel and oxidizer together in close proximity, including sputter deposition [1], and arrested milling methods [2]. In this paper, we demonstrate an electrospray route to assemble Al and CuO nanoparticles into micron composites with a small percentage of energetic binder, which shows higher reactivity than nanothermite made by conventional physical mixing. The electrospray approach offers the ability to generate microscale particles with a narrow size distribution, which incorporates an internal surface area roughly equivalent to the specific surface area of a nanoparticle. The size of the micron scale composites could be easily tuned by changing the nitrocellulose content which is used as the binder. The composites were burned in a confined pressure cell, and on a thin rapidly heated wire to observe b
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Volume: 186 Issue: 9 First Page #: 0
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Publication Location:
**Article Title:** Initiation and Reaction in Al/Bi Bi2O3 Nanothermites: Evidence for the; Predominance of Condensed Phase Chemistry
**Authors:**
**Keywords:** Energetics
**Abstract:** This study explores the reaction between Al and Bi2O3 nanoparticles under high heating rate conditions with temperature-jump/time of flight mass spectrometry (T-Jump/TOFMS), high speed imaging, and rapid sample heating within a scanning electron microscope (SEM). Comparison of rapid heating of Al/Bi2O3 thermite and neat Bi2O3 shows that initiation of the Al/Bi2O3 reaction occurs at a much lower temperature than the point where oxygen is released from the neat Bi2O3 powder. Thus, without the presence of a gas phase oxidizer, it can be concluded that a condensed phase initiation mechanism must be at play in the Al/Bi2O3 nanothermite. C/Bi2O3 heating experiments were used for a mechanistic comparison between two different fuel types since the carbon represents a nonvolatile fuel in contrast to the aluminum. This formulation showed a similar condensed phase initiation as was seen with the aluminum nanothermite. Qualitative comparison of high speed imaging for Al/Bi2O3 and Al/CuO indicates
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**Paper Title:** Microsphere Composites of Nano-Al and Nonothermites: An approach to Better Utilization of Nanomaterials
**Authors:** Haiyang Wang1 , Guoqiang Jian2 , Jeffery B. DeLisio2 , and Michael R. Zachariah
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**Conference Name:** 54th AIAA Aerospace Sciences Meeting
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Conference Location: San Diego, California, USA
**Paper Title:** Size-Resolved Burn Rate Measurements of Metal NanoParticles
**Authors:** R. Jacob, Y, Zong, Y. Yang, S. Li and M.R. Zachariah
Acknowledged Federal Support: **Y**

# Accomplishments

- **Super-reactive Nanoenergetic Gas Generators based on Periodate Salts**

While aluminum is the most widely used fuel, there are a wide range of potential oxidizers with various properties. In this report, we have prepared periodate salt ($KIO_4$ and $NaIO_4$) nanoparticles which are known to have low toxicity and hygroscopicities, but extremely high oxidative power. Our results show that when formulated into nanocomposites with aluminum, periodate nanoparticles demonstrate highly reactive properties as well as superior gas generating behavior (the best performance known so far). Several in-situ techniques at high heating rates as well as TG-DSC have been employed to probe the reaction mechanisms. The results suggest that exothermic decomposition of periodate salts contributes to the low ignition temperature of its nanoenergetic formulations. This study also shows, for the first time, clear evidence to support that direct gas phase oxygen release, from oxidizers in a nanoenergetic formulation is responsible for the combustion performance.

- **Condensed Vs. Gas Phase Reactions**

We employ a variety to studies to understand the relative role of vapor vs, condensed state reaction in nanothermites. We studied the reaction between Al and Bi2O3 nanoparticles under high heating rate conditions with temperature-jump/time of flight mass spectrometry (T-Jump/TOFMS), highspeed imaging, and rapid sample heating within a scanning electron microscope (SEM).Comparison of rapid heating of Al/Bi2O3 thermite and neat Bi2O3 shows that initiation ofthe Al/Bi2O3 reaction occurs at a much lower temperature than the point where oxygen isreleased from the neat Bi2O3 powder. Thus, without the presence of a gas phase oxidizer, it can be concluded that a condensed phase initiation mechanism must be at play in the Al/Bi2O3 nanothermite. C/Bi2O3 heating experiments were used for a mechanistic comparison between two different fuel types since the carbon represents a nonvolatile fuel in contrast to the aluminum. This formulation showed a similar condensed phase initiation as was seen with the aluminum nanothermite. Qualitative comparison of high speed imaging for Al/Bi2O3 and Al/CuO indicates that the initiation reaction in Al/Bi2O3 is about twice as fast as a comparable copper oxide system, which has not been apparent from bulk thermite combustion studies. Bi2O3 is known to possess unique ion transport properties, which combined with the presence of oxygen and aluminum ions within the nanothermite system mayplay a significant role in the speed of the nanothermite reaction.

We also examine the combustion product particles of three nano-sized thermite systems (Al/CuO, Al/$WO_3$, Al/$Bi_2O_3$) as a probe of the underlying mechanism. Electron Microscopy (EM) and Energy-dispersive X-ray Spectroscopy (EDX) were used to evaluate the combustion product particle size distribution and composition. The results show two distinct product particle size distributions common to all three oxidizers. The larger particles are super-micron (though the precursors were nano-sized) and comprise approximately 90% of the product mass. Simple scaling arguments show that the large population cannot be formed from the vapor given the available residence time. The smaller distribution is sub-100 nm which is primarily the reduced metal formed from vapor phase condensation. This result implies that the majority of the global reaction and thus the energy release is occurring in the condensed phase. Based on these results, a phenomenological mechanism for the nanoaluminum based thermite reaction is proposed. These results all point to a rapid loss of surface ( nanostructure). It is axiomatic that the burning time dependence on particle size follows an integer power law dependence. However, a considerable body of experimental data show a power dependence less than unity. In this paper, we focus on what might be responsible for the fractional power dependence observed for the burning time for nanoaparticles ( e.g. Al and B). Specifically we employ reactive molecular dynamics simulations of oxide-coated aluminum nanoparticles (Al-NPs). Since most nanomaterials experimentally investigated are aggregates, we study the behavior of the simplest aggregate – a doublet of two spheres. The thermo-mechanical response of an oxide coated Al-NP is found to be very different than its solid alumina counterpart, and in particular we find that the penetration of the core aluminum cations into the shell significantly softens it, resulting in sintering well below the melting point of pure alumina. For such coated nanoparticles, we find a strong induced electric field exists at the core-shell interface. With heating, as the core melts, this electric field drives the core Al cations into the shell. The shell, now a sub-oxide of aluminum, melts at a temperature that is lower than the melting point of aluminum oxide. Following melting, the forces of surface tension drive two adjacent particles to fuse. *The characteristic sintering time (heating time + fusion time) is seen to be comparable to the characteristic reaction time, and thus it is quite possible for nanoparticle aggregates to sinter into structures with larger length scales, before the bulk of the combustion can take place.* This calls into question what the appropriate 'effective size' of nanoparticle aggregates is.

- ***In situ* evidence for ultra-fast loss of nanostructure in nanoparticle aggregates and how to mitigate this effect.**

Building on our prior work on loss of surface are in nanoaluminum we turn our attention to thermite reactions. The reaction between metallic fuel and oxygen carriers is investigated through ultra–fast laser heating of aluminum and copper oxide (CuO) nanoparticles (NPs) using Movie Mode Dynamic Transmission Electron Microscopy (MM-DTEM) enabling high spatial and temporal resolution. Nanothermite materials heated *in situ* at ~$10^{11}$ K/s showed significant morphological changes on timescales of 1-5 μs. The resulting structures were typically phase-separated into adjoining spheroids. Further analysis with energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED) was used to determine the extent of reaction. Bulk scale reaction experiments using temperature jump wire heating (~$10^5$K/s) revealed that both the reaction products and general processes were comparable to the reactions driven by the DTEM laser heating. These results indicate that condensed phase and interfacial reactions are the fast and dominant mechanisms in the nanothermite combustion.

To deal with the prowe demonstrate an electrospray route to assemble Al and CuO nanoparticles into micron composites with a small percentage of energetic binder, which shows higher reactivity than nanothermite made by conventional physical mixing. The electrospray approach offers the ability to generate micro scale particles with a narrow size distribution, which incorporates an internal surface area roughly equivalent to the specific surface area of a nanoparticle. The size of the micron scale composites could be easily tuned by changing the nitrocellulose content which is used as the binder. The composites were burned in a confined pressure cell, and on a thin rapidly heated wire to observe burning behavior. The sample of 5 wt. % nitrocellulose showed the best response relative to the physical mixing case, with a 3X higher pressure and pressurization rate. The ignition characteristics for these micron particles are essentially equivalent to the nanothermite despite their significantly larger physical size. It appears that electrospray assembly process offers to potential advantages. 1. Enhanced mixing between fuel and oxidizer; 2. Internal gas release from nitrocellulose that separates the particles rapidly to prevent sintering. The later point was shown by comparing the product particle size distribution after combustion.

- **Evaluating free vs. bound oxygen on ignition of nano-aluminum based energetics leads to a critical reaction rate criterion**

We investigated the ignition of nano-aluminum (n-Al) and n-Al based energetic materials (nanothermites) at varying $O_2$ pressures (1-18 atm), aiming to differentiate the effects of free and bound oxygen on ignition and to assess if it is possible to identify a critical reaction condition for ignition independent of oxygen source. Ignition experiments were conducted by rapidly heating the samples on a fine Pt wire at a heating rate of $\sim 10^5$ ˚C $s^{-1}$ to determine the ignition time and temperature. The ignition temperature of n-Al was found to reduce as the $O_2$ pressure increased, whereas the ignition temperatures of nanothermites (n-Al/$Fe_2O_3$, n-Al/$Bi_2O_3$, n-Al/$K_2SO_4$ and n-Al/$K_2S_2O_8$) had different sensitivities to $O_2$ pressure depending on the formulations. A phenomenological kinetic/transport model was evaluated to correlate the concentrations of oxygen both in condensed and gaseous phases, with the initiation rate of Al-O at ignition temperature. We found that a constant critical reaction rate ($5\times10^{-2}$ mol $m^{-2}$ $s^{-1}$) for ignition exists which is independent to ignition temperature, heating rate and free vs. bound oxygen. Since for both the thermite and the free $O_2$ reaction the critical reaction rate for ignition is the same, the various ignition temperatures are simply reflecting the conditions when the critical reaction rate for thermal runaway is achieved.

- **Size Resolved High Temperature Oxidation Kinetics of Nano-Sized Titanium and Zirconium Particles**

While ultrafine metal particles offer the possibility of very high energy density fuels, there is considerable uncertainty in the mechanism by which metal nanoparticles burn, and few studies that have examined the size dependence to their kinetics at the nanoscale. In this work we quantify the size dependence to the burning rate of titanium and zirconium nanoparticles. Nanoparticles in the range of 20-150 nm were produced via pulsed laser ablation, and then in-flight size-selected using differential electrical mobility. The size-selected oxide free metal particles were directly injected into the post flame region of a laminar flame to create a high temperature (1700 - 2500K) oxidizing environment. The reaction was monitored using high-speed videography by tracking the emission from individual nanoparticles. We find that sintering occurs prior to significant reaction, and that once sintering is accounted for, the rate of combustion follows a near ~ (diameter)1 power-law dependence. Additionally, Arrhenius parameters for the combustion of these nanoparticles were evaluated by measuring the burn times at different ambient temperatures. The optical emission from combustion was also used to model the oxidation process, which we find can be reasonably described with a kinetically controlled shrinking core model.

- **Probing the Reaction Dynamics of Thermite Nanolaminates**

In collaboration with the group of Jon-Paul Maria at NC-State, Al/CuO reactive nanolaminate ignition was studied using temperature jump (T-Jump) heating for rates greater than 105 K/s.

Multilayer samples were sputter deposited onto thin platinum filaments in alternating layers of Al and CuO. The filaments were resistively heated in a time of flight mass spectrometer (ToF-MS) while ignition and reaction were observed with high-speed video. A total deposited thickness of 1800 nm was maintained for all samples while the number of bilayers was varied from 1 to 12. Increasing this value decreased the diffusion distances and increased the amount of interfacial area across which reaction could occur, while keeping the overall energy of the system constant. From 2 to 6 bilayers the ignition temperature decreased from 1250 K to 670 K and the overall reactivity increased. Past 6 bilayers, the ignition temperature only decreased slightly and there was little impact on the overall reactivity. This behavior is consistent with a mass-transport model where the predominant diffusing species exhibits a low activation energy (50 kJ/mol). Ignition temperature, which depends upon bilayer thickness, is found to be a good predictor of flame speed.

- **Heat Transfer Mechanisms in Nanothermite Propagation**

The combustion of nanothermites is a complex multiphase process that is still not well understood. One important aspect that is in need of further examination is the heat transfer mechanisms that drive combustion. Here we present some simple calculations to critically analyze the viability of conduction, convection, and radiation mechanisms of heat transfer as it relates to reaction propagation in nanothermites. While convection has generally been accepted as the critical mechanism for heat transfer, we show that the movement of hot gases cannot account for the required energy flow. Instead, it is illustrated that the movement of condensed phase material plays the critical role in heat transfer and should be accounted for in future models.

- **Oxygen-ion Conductivity as a Metric for Ignition**

Nanothermites offer high energy density and high burn rates, but are mechanistically only now being understood. One question of interest is how initiation occurs and how the ignition temperature is related to microscopic controlling parameters. In this study, we explored the potential role of oxygen mobility in the oxidizer as a controlling mechanism. Five different doped bismuth oxides with a constant dopant ratio of 15mol% were synthesized by aerosol spray pyrolysis. The ignition temperatures of Al/doped $Bi_2O_3$, C/doped $Bi_2O_3$ and Ta/ doped $Bi_2O_3$ were measured by temperature-jump/time-of-flight mass spectrometer coupled with a high-speed camera. These results were then correlated to the corresponding oxygen ion conductivity for these doped $Bi_2O_3$ measured by impedance spectroscopy between 200 and 750 °C. We find that ignition occurs at a critical oxygen ion conductivity (~0.06 S/cm) in the condensed-phase so long as the aluminum is in a molten state. Similar critical oxygen ion conductivity was also found for the ignition of carbon and tantalum based thermites. These results suggest that a critical transport limit in the condensed state thermite ignition is oxygen ion-transport.

- **Ignition and Combustion Characteristics of Nanoaluminum with Copper Oxide Nanoparticles of Differing Oxidation State**

The importance of oxidation state of an oxidizer and its impact on gaseous oxygen and total gas production in nanocomposite thermite combustion was investigated by probing the reaction and ignition properties of aluminum nanoparticles (Al-NPs) with both cupric oxide (CuO) and cuprous oxide (Cu2O) nanoparticles. The gas release and ignition behavior of these materials were tested with >105 K/s temperature jump (T-jump) heating pulses in a high temporal resolution time of flight mass spectrometer (ToF-MS) as well as in an argon environment. Reactivity was tested using a constant volume combustion cell with simultaneous pressure and optical measurements. A variety of Cu2O particle sizes ranging from 200-1500 nm were synthesized and found to release oxygen at ~1200 K, which is higher than the values found for a variety of CuO particle sizes (~1000 K). Both oxides were found to ignite around 1000 K, which implies a consistent ignition mechanism for both through a condensed phase pathway. The higher oxidation state (CuO) thermites were found to react faster and produce higher pressures by several orders of magnitude, which implies that gaseous species play a critical role in the combustion process. Differences in reactivity between argon and vacuum environments and the use of Cu diluent to simulate Cu2O, suggest that it is the intermediate product gas, O2, that plays the most significant role in combustion as an enabler of heat transfer and a secondary oxidizer. The lack of any oxidizer size dependence on ignition is suggestive of rapid sintering that wipes out the effect of enhanced interfacial contact area for smaller oxidizers.

- **Doped Perovskites to Evaluate the Relationship between Fuel-Oxidizer Thermite Ignition and Bond Energy, Electronegativity and Oxygen Vacancy**

Despite our knowledge of the existence of the violent thermite reaction for over 100 years it is still not yet understood how the properties of a metal oxide oxidizer relate too and influence the ignition temperature. To address this shortcoming we prepared a series of perovskite based oxidizers which enable a systematic investigation of how materials properties of the oxidizer relate to the ignition temperature. In this paper, nine lanthanum based perovskites with different Sr2+ doping of the A-site, and different B-site transition metals were synthesized. The perovskite O2 release and ignition temperatures with aluminum were measured by fast heating (> 105 K/s) temperature-jump/time-of-flight mass spectrometry coupled with high-speed imaging. These results were then correlated with the average bond energy and overall metal-oxygen electronegativity difference. Remarkably we found a linear relationship between average bond energy and electronegativity with ignition temperature. To our knowledge this is the first demonstration of the connection between metal–oxygen bond energy, electronegativity and ignition temperature.

- **High Heating Rate Reaction Dynamics of Al/CuO Nanolaminates by Nanocalorimetry-Coupled Time-of-Flight Mass Spectrometry**

Highly tunable reactive nanolaminates have been of recent interest for various “on chip” energetic applications. The reaction dynamics of Al/CuO nanolaminates were investigated by nanocalorimetry-coupled time-of-flight mass spectrometry, capable of simultaneous measurement of temporal thermal dynamics and detection of evolved gas phase species at heating rates up to ≈ 106 K/s. The nanolaminates were synthesized by alternately sputtering Al and CuO onto the heater of nanocalorimeter sensors. For thin films of 80 nm with one bilayer, the stiochometric ratio of fuel to oxidizer significantly affected the reaction mechanism: initial reactions occurred between 300 °C and 400 °C, and main reactions varied based on stoichiometry. For thicker films of 199 nm and 266 nm, a series of samples with varying bilayer numbers were analyzed to determine the effect of diffusion distance and interfacial area. Only one reaction step was observed for a sample with a bilayer thickness of 33 nm. A two-step reaction mechanism is observed as the bilayer thickness was increased to 66 nm and beyond: purely condensed phase reaction occurring at the interfaces of Al and CuO before the melting of Al and a much faster liquid-solid reaction right after the melting of Al. At the same time, interfacial premixed distance during the deposition was also estimated from parallel experiments. Furthermore, the power data from nanocalorimetry provides a more accurate method to determine the ignition temperature and actual energy output of these systems.

- **Oxidizers Control Ignition Regardless of Fuel**

The redox reaction between fuel (metal, metalloid, etc.) and metal oxide is ubiquitous. On the other hand simple thermodynamic considerations do not seem to yield much insight into what makes for a vigorous oxidizer. In this study, two different systematic doped metal oxides: perovskites (9 compounds) and $\delta$-$Bi_2O_3$ (12 compounds) were synthesized in a manner such that for each system the crystal structure and morphology were maintained. Four fuels (Al, B, Ta, C) with different physical properties were included in this study. The initiation temperature and oxygen release temperature was measured by fast heating ($> 10^5$ K/s) temperature-jump/time-of-flight mass spectrometry coupled with high-speed imaging. These results were then correlated with the average metal-oxygen bond energy in the oxidizer, and overall metal-oxygen electronegativity. In general, within each systematic metal oxide, we found linear relationships between average bond energy and electronegativity of the metal oxides with initiation temperature for all four fuels, despite their very different physical/chemical properties. These results indicate that intrinsic atomic properties of metal oxide control fuel-metal oxide reaction initiation.

- **High Heating Rate Decomposition Dynamics of Copper Oxide by Nanocalorimetry-Coupled Time-of-Flight Mass Spectrometry**

Copper oxide (CuO) can be thermally decomposed to release oxygen and is often used as an oxidizer for reactive composites and in chemical looping combustion. Reactive composites release energy rapidly, therefore the energetics of these reactions should be studied at high heating rates that represent combustion timescales. A recently developed nanocalorimetry-coupled time-of-flight mass spectrometry system is capable of simultaneous measurement of temporal thermal dynamics and evolved gas phase species at heating rates up to ~$10^6$ K/s. This approach can be used to measure the dynamics of CuO decomposition and oxygen evolution, which is critical to understanding the role of CuO as an oxidizer in reactive mixtures and important for designing new reactive materials, whether they be mixtures of nanoparticles or nanolaminates. Previous studies based on time-of-flight mass spectrometry showed only one oxygen release event during decomposition at high heating rates, and two decomposition events at slow rates. Using nanocalorimetry-coupled time-of-flight mass spectrometry, it has been confirmed that CuO decomposes by two steps at both slower heating and higher heating rates, measured up to ~$10^5$ K/s. The two decomposition steps influence the reaction course in the reactive composites using CuO as an oxidizer, and further understanding is important in designing these materials.

- **Incomplete reactions in nanothermite composites**

Exothermic reactions between oxophilic metals and transition/ post transition metal-oxides have been well documented owing to their fast reaction time scales (≈ 10 μs). This article examines the extent of reaction in nano-aluminum based thermite systems through a forensic inspection of the products formed during reaction. Three nanothermite systems (Al/CuO, Al/$Bi_2O_3$ and Al/$WO_3$) were selected owing to their diverse combustion characteristics thereby providing sufficient generality and breadth to the analysis. Microgram quantities of the sample were coated onto a fine platinum wire, which was resistively heated at high heating rates (≈ $10^5$ K/s) to ignite the sample. The subsequent products were captured/quenched very rapidly (≈ 500 μs) in order to preserve the chemistry/morphology during initiation and subsequent reaction and were quantitatively analyzed using electron microscopy (EM), focused ion beam (FIB) cross-sectioning followed by energy dispersive X-ray spectroscopy (EDX). Elemental examination of the cross-section of the quenched particles show oxygen predominantly localized in the regions containing aluminum, implying the occurrence of redox reaction. The Al/CuO system, which has simultaneous gaseous oxygen release and ignition ($T_{Ignition} \approx T_{Oxygen\ Release}$), shows substantially lower oxygen content within the product particles as opposed to Al/$Bi_2O_3$ and Al/$WO_3$ thermites, which are postulated to undergo a condensed phase reaction ($T_{Ignition} << T_{Oxygen\ Release}$). An effective Al:O composition for the interior section was obtained for all the mixtures, with the smaller particles generally showing higher oxygen content than the larger ones. The observed results were further corroborated with the reaction temperature, obtained using a high-speed spectro-pyrometer, and bomb calorimetry conducted on larger samples (≈ 15 mg). The results suggest that thermites that produce sufficient amounts of gaseous products generate smaller product particles and achieve higher extents of completion.

- **Boron Ignition and Combustion with Doped δ-$Bi_2O_3$: Bond energy/Oxygen Vacancy Relationships**

To extract a clearer relationship between atomic properties of the oxidizer, and ignition temperature and combustion kinetics. Pure $Bi_2O_3$ and a series of $Y^{3+}$ and $W^{6+}$ doped $Bi_2O_3$ nanoparticles with the same crystal structure and morphology were synthesized via aerosol spray pyrolysis and used as oxidizers in boron-based thermites. This enabled us to vary bond energy and oxygen vacancy concentration systematically. The ignition temperatures and the reactivity of different B/$Bi_2O_3$ thermites were measured by rapid heating (>$10^5$ K/s) temperature-jump/time of flight mass spectroscopy and a confined pressure cell, respectively. With pure $Bi_2O_3$, the boron can be ignited at a temperature as low as 520 °C. In-situ high heating rate TEM was used to observe the reaction before/after heating. We find very clear relationships, that higher oxygen vacancy concentration and smaller metal-oxygen bond energy lead to lower ignition temperature and higher combustion reactivity.

- **Assembly and Encapsulation of Aluminum NP's within AP/NC Matrix and their Reactive Properties**

Aluminum nanoparticles (Al NPs) are commonly employed as fuel supplement to increase the energy density of propellants. However, due to the highly agglomerated state of the NPs and significant pre-combustion sintering, ignition and combustion are not as facile as they could be. In this work, we employed a spray approach to generate near monodisperse microparticles of Al NP's encapsulated within ammonium perchlorate (AP) and a binder (nitrocellulose (NC)) The results show that Al/AP/NC composites have an ignition temperature (~700 K), which is significantly lower than Al melting point (~933 K). The reactivity of Al/AP/NC composites was also tested in a confined cell where we find that although the peak pressure for Al/AP/NC is comparable to that of physically mixed Al/CuO nanothermite, the impulse generated is more than two times higher. The measured flame temperature of Al/AP/NC composites were as high as 2800 K, which is ~500 K higher than Al/AP composites without NC. Furthermore, the potential mechanism for the early ignition of these composites were investigated. It is proposed that gaseous acid released from AP could play an important role in weakening the protective oxide shell on Al nanoparticles which could subsequently lead to the reaction of Al in the high-pressure oxygenated environment at lower temperature.

- **Investigating the Oxidation Mechanism of Tantalum Nanoparticles at High Heating Rates**

Reduced diffusion length scales and increased specific surface areas of nanosized metal fuels have recently demonstrated increased reaction rates for these systems, increasing their relevance in a wide variety of applications. The most commonly employed metal fuel, aluminum, tends to oxidize rapidly near its melting point (660 $^{o}$C) in addition to undergoing a phase change of the nascent oxide shell. To further expand on the understanding of nanosized metal fuel oxidation, tantalum nanoparticles were studied due to their high melting point (3017 $^{o}$C) in comparison to aluminum. Both traditional slow heating rate and *in-situ* high heating rate techniques were used to probe the oxidation of tantalum nanoparticles in oxygen containing environments in addition to nanothermite mixtures. When oxidized by gas phase oxygen, the oxide shell of the tantalum nanoparticles rapidly crystallized creating cracks that may attribute to enhanced oxygen diffusion into the particle. In the case of tantalum based nanothermites, oxide shell crystallization was shown to induce reactive sintering with the metal oxide resulting in a narrow range of ignition temperatures independent of the metal oxide used. The oxidation mechanism was modeled using the Deal-Grove model to extract rate parameters, and theoretical burn times for tantalum based nanocomposites were calculated.

- **Quantifying the effect of micro-structure on reactivity of assembled nanothermite composites**

  Exothermic reactions between nanoscale metal/metal oxide systems are of importance in the field of energetics owing to their fast reaction timescale, high energy density and tunability. In this work, we tune the reactivity of nanothermite composites by assembling them into gelled microspheres incorporating nitrocellulose as binder/gas generator via one step electrospray (ES) synthesis and compare their performance enhancement with physically mixed counterparts. Stoichiometric blends of three different nanothermite composites (Al/CuO, Al/$WO_3$ and Al/$Fe_2O_3$) were synthesized and tested in this study to highlight the generality of the synthesis procedure. The reactivity of the sample was gauged by simultaneously recording the pressure and optical emission signals from the nanothermite reaction, ignited in an inert environment within a constant volume combustion cell. The optical emission was spectrally and temporally resolved (at ~350 kHz) using a high-speed spectrometer to obtain time resolved gray body temperature while the heat of reaction was evaluated by bomb calorimetry in an inert environment. The results show that the ES assembled composites, owing to their characteristic in situ gas generation from nitrocellulose decomposition, significantly outperform their physically mixed counterparts and achieve higher extents of completion. The nitrocellulose not only acts as a binder but also as a dispersant, de-aggregating the composite prior to reaction, thereby reducing extensive coalescence. Moreover, the tunability of the ES assembled composite structure was further demonstrated by altering the solids loading of the composites. Results indicate that a more open/porous composite structure resulting from low solids loading in precursor demonstrated enhanced combustion performance, highlighting the significance of advective heat and mass transport on the overall reactivity.

- **Pre-stressing nanoparticles as a strategy to enhance reactivity of nanothermite composites**

Aluminum (Al) fuel particles are used in a variety of energetic formulations yet harvesting their full chemical potential energy and increasing their energy release rate upon ignition have been a challenge and are key motivators to advancing energy generation technologies. One approach to improving combustion performance is to alter the mechanical properties of the Al particle by inducing an elevated stress state through prestressing. This study examines the combustion performance of prestressed nanoscale aluminum (nAl) particles that were annealed to temperatures ranging from 200-400°C and quenched at slow (exponential) and faster (linear) cooling rates. Powder X-ray diffraction measurements show that prestressing nAl particles at 300°C annealing temperature induces an order of magnitude increase in strain. Constant volume combustion cell tests on nAl combined with copper oxide nanopowder (nAl+CuO) revealed higher peak pressures and pressurization rates for prestressed nAl+CuO composites compared to their untreated counterpart. High speed emission spectroscopy was employed to deduce condensed phase temperatures from the reaction front Burn time measurements, obtained from integrating the emission intensity, were observed to correlate inversely with pressure. High heating rate (~5x$10^5$ K/s) *in-situ* TEM results augment the combustion cell results. The results imply that prestressing mechanically alters the nanoparticles which subsequently accelerates the release of aluminum core through outward diffusion. This results in the rapid loss of nanostructure which was observed at the nanoscale through *in-situ* electron microscopy. The released aluminum thus reacts with the oxide in the condensed phase resulting in a faster and more violent reaction. Improved performance of prestressed nAl coupled with the simplicity of processing provides a low cost and scalable approach to improving metal fuel particle combustion.

- **What atomic properties of metal oxide control the reaction threshold of solid elemental fuels?**

The redox reaction between fuel (metal, metalloid, etc.) and metal oxide is ubiquitous. On the other hand simple thermodynamic considerations do not seem to yield much insight into what makes for a vigorous oxidizer. In this study, two different systematically doped metal oxide systems: perovskites (9 compounds) and $\delta$-$Bi_2O_3$ (12 compounds) were synthesized in a manner such that for each system the crystal structure and morphology were maintained. Four fuels (Al, B, Ta, C) with different physical properties, covering almost all fuel types, were included in this study. The initiation temperature and oxygen release temperature was measured by fast heating (> $10^5$ K/s) temperature-jump/time-of-flight mass spectrometry coupled with high-speed imaging. These results were then correlated with the average metal-oxygen bond energy in the oxidizer, and overall metal-oxygen electronegativity. In general, within each systematic metal oxide, we found linear relationships between average bond energy and electronegativity of the metal oxides with initiation temperature for all four fuels, despite their very different physical/chemical properties. These results indicate that intrinsic atomic properties of metal oxide control fuel-metal oxide reaction initiation.

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