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LLNL-TR-716603

In Situ Imaging of Particle Formation and Dynamics in Reactive Material Deflagrations

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January 4, 2017

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

In situ imaging of particle formation and dynamics in reactive material deflagrations

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Abstract

Reactive composites utilizing nanoparticles have been the topic of extensive research in the past two decades. The driver for this is that, as the particle size is decreased, the mixing scale between constituents is greatly reduced, which has long thought to increase the rate of chemical reaction. While a general trend of increased reactivity has been seen for metal / metal oxide, or thermite, reactive materials, some results have demonstrated diminishing returns as the particle size is further decreased. Recent results have shown that nanoparticles, which are typically aggregates of several primary particles, can undergo very rapid coalescence to form micron particles once a critical temperature is reached. Experiments on this topic to date have been performed on very small sample masses, and sometimes under vacuum; conditions which are not representative of the environment during a deflagration. In this feasibility study, a custom burn tube was used to ignite and react 100 mg powdered thermite samples in long acrylic tubes. X-ray imaging at APS Sector 32 was performed to image the particle field as a function of distance and time as the rarefied particle cloud expanded and flowed down the tube. Five different thermite formulations were investigated, Al / CuO, Al / Fe2O3, Al / SnO2, Al / WO3, and Al / Fe2O3, along with Al / CuO formulations with different sizes of Al particles ranging from 80 nm to approximate 10 μm. The results clearly show that the sample powder reacts and unloads into a distribution of larger micron-scale particles (~5-500 μm), which continue to react and propagate as the particle-laden stream flows down the tube. This was the first direct imaging of the particle field during a thermite deflagration, and gives significant insight into the evolution of reactants to products. Analysis of phase is currently being pursued to determine whether this method can be used to extract reaction kinetics.

Background and Research Objectives

Thermites are mixtures of a metal and a metal oxide, which exothermically react upon ignition to release chemical energy in the form of heat and / or pressure. The classical use of thermite dates back to 1904 and involved the reaction between metallic aluminum and iron oxide (Fe2O3) to produce molten iron metal to weld railroad ties together in Hungary. This method is commonly referred to as the Goldschmidt method, named after the German chemist Hans Goldschmidt. In 1995, Aumann et al. (1995) demonstrated that the reactivity in thermite formulations of Al / MoO3 was observed to be dramatically increased by over three orders of magnitude when nanoparticles were used in place of micron-sized constituents. Additionally, thermochemical calculations

performed by Fischer and Grubelich (1996) showed that some formulations of thermite have a higher mass and / or volumetric energy density than even CL-20, one of the highest power explosives used today. In energetic material applications, it is the rate of energy release, or power, of the chemical reaction which ultimately quantifies its performance and application space.

By using nanoparticles, it has long been thought that the power in thermites could be increased to a level in which these materials could be competitive with high explosive (HE) applications. However, there have been several recent studies showing diminishing returns in reactivity with particle size. Authors have suggested that a problem with nanoparticles, which are typically aggregated, is that upon melting the surface tension forces serve to drive particles to coalesce into larger particle sizes. This has been directly measured by Egan et al. (2014) to occur in Al aggregates in as little as 25 ns using the dynamic transmission electron microscope (DTEM) at LLNL. This morphology change results in a decreased surface area, and has been thought to limit reactivity. Dynamic measurements like this yield valuable information of the length and time scales associated with reaction, however, are difficult to make due to the fine spatial and time scales associated with these processes.

In this work, the primary goal was to directly image the reaction of a thermite during a deflagration using the collimated X-ray beamline at the Advanced Photon Source (APS, Sector32). A 100 mg sample of thermite powder was ignited in a long, clear tube and allowed to flow one-directionally down the tube as it reacted. The time-resolved particle field was then imaged perpendicular to the direction of flow, and at various distances down the tube corresponding to different times after initiation. The imaging technique allowed us to measure the unloaded particle size and, additionally, to observe phase and dynamics occurring within these particles as the reaction proceeded. The results are the very first of their kind, and significantly enhance our understanding of the dynamics occurring in thermites.

Scientific Approach and Accomplishments

An LLNL-developed method for testing the reactivity of thermites was used in this work. The experimental setup is shown in Figure 1, and has been termed the “extended burn tube” (EBT) test by Sullivan et al. (2015). A 100 mg powdered charge of a thermite is loaded into the closed end of a long, acrylic tube. An ignition wire is inserted into the powder, and resistively heated with a fast current pulse. This ignites the material, which subsequently leads to unloading and flow of a rarefied powder cloud as the material reacts and expands one-directionally down the tube. It is assumed that there is a direct linkage between spatial position down the tube, and reaction time. X-ray imaging was performed normal to the flow direction, and time-resolved movies of the particle field were measured. The tube could then be translated, and the experiment repeated to look at different positions. Due to the high reproducibility of the burn tube experiment, the results could be stitched together from separate experiments to draw conclusions of the overall deflagration.

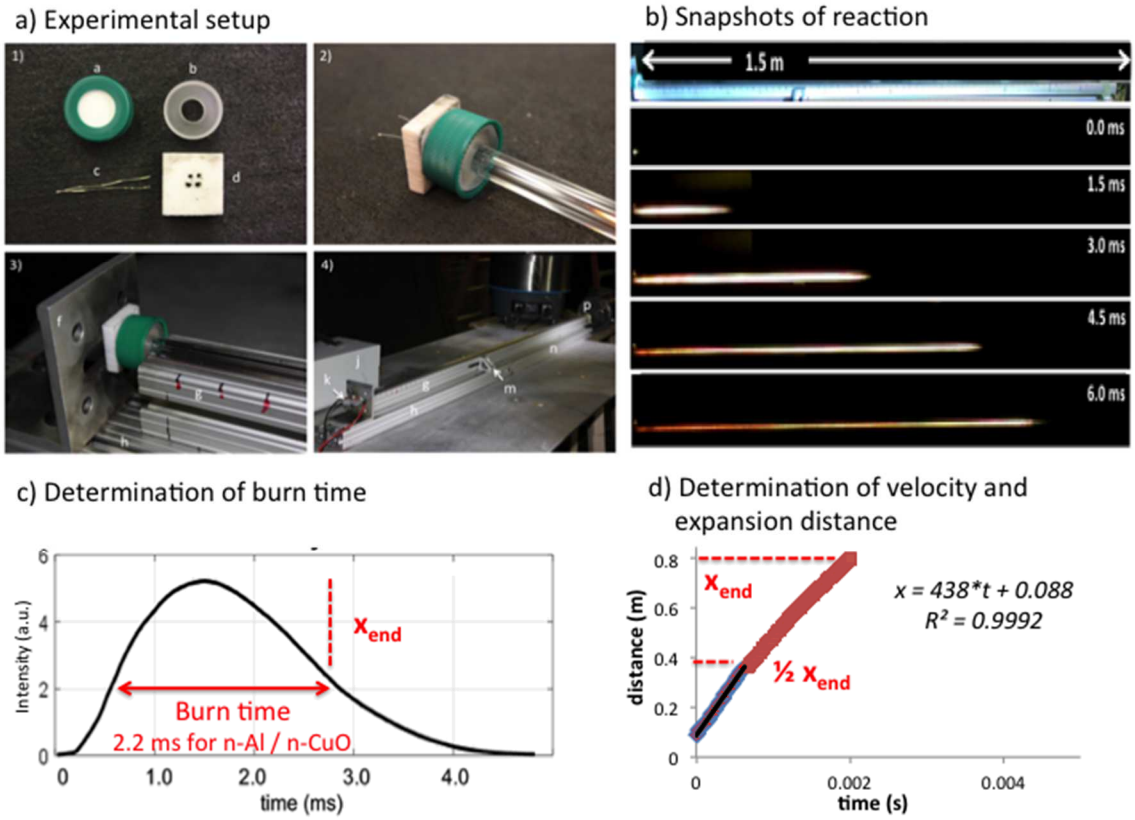

Figure 1: a) Schematic of the EBT test. b) Still shots of the reaction igniting and propagating down the tube. c) Analysis of burn time by plotting the optical intensity vs. time and measuring the full width at half max of the intensity. d) Analysis of the flow velocity and quenching distance.

The EBT setup was brought to APS twice over the lifetime of this project, once in March 2016 when the beam was operating in 24-bunch mode and once in July 2016 while the beam was in hybrid-singlet mode. In 24-bunch mode, we found the beam intensity was insufficient to yield high quality images from a single pulse. Instead, multiple exposures were required but, due to the high particle velocity in the tube, this led to blurring of the images. In the second visit, the beam was in hybrid-singlet mode and provided sufficient energy to image from a single pulse. A schematic of the experimental setup is shown in Figure 2. X-ray imaging was performed perpendicular to the flow, and a high-speed camera was used to record the luminous streak as it flows down the tube. The tube was translated to image at different positions after initiation.

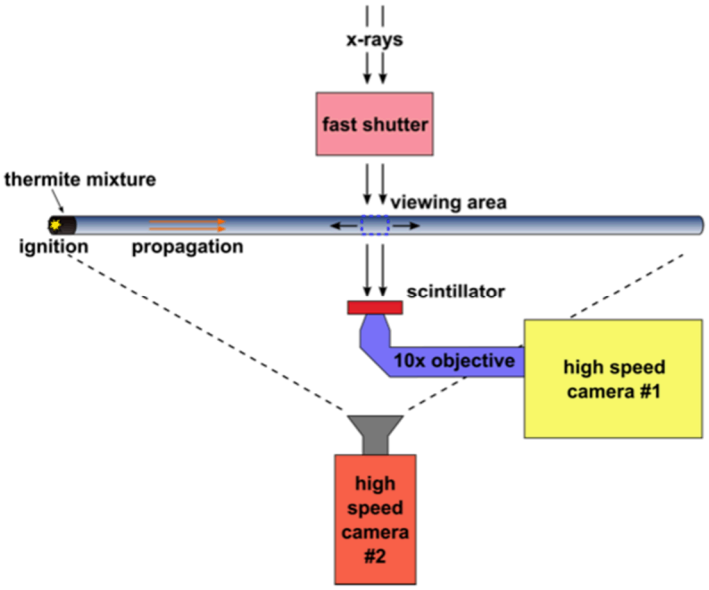

Figure 2: Schematic of experimental setup at APS. The reaction is initiated at the end of the tube, and the X-ray imaging is performed normal to the direction of flow.

Several representative images of the collected data are shown in Figure 3. A time-resolved sequence of the Al / Fe2O3 reaction is shown, and one can see the formation of large, spherical particles as the powder unloads and rarefies. Within the particles, one can observe the evolution of dark regions which are, presumably, the formation and phase-separation of the molten Fe product from the molten Al2O3. Four different thermite images collected at late times after ignition are shown as well. One common observation is that all particles are much larger than the initial, nanometric, particle sizes used in the formulations. Additionally, one can observe morphological differences in the particles for different formulations. In particular, the Al / WO3 system appears most irregular in shape, and we hypothesize this is due to the high melting point of the tungsten product, which hinders flow and phase separation. Finally, we observed some dynamic phenomena such as the formation and collapse of gas bubbles within these particles (also shown in Figure 3).

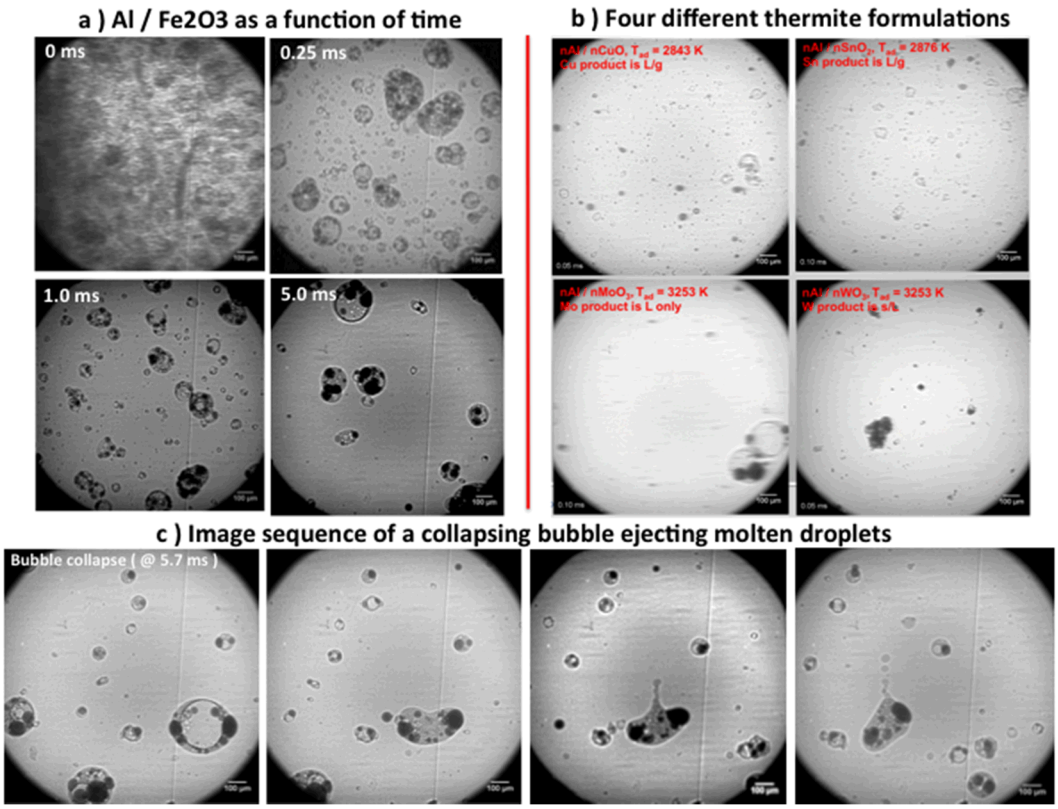

Figure 3: a) Time-resolved sequence of Al / Fe2O3 thermite. b) Comparison of different thermites in the unloaded state. c) Image sequence showing the dynamic collapse of a bubble in Al / Fe2O3.

Due to the very large number of samples and images collected at APS, it was necessary to automate the data analysis. The movies were processed by first background subtracting a blank movie from the image deck. An edge-finding routine was then performed using ImageJ to outline the particles, upon which the average particle diameter could then be extracted. The number, area, and volume-averaged particle diameter were all measured, however, the volume-averaged diameter was chosen for reporting as it represents the average particle size with respect to mass, which is most relevant. The sample analysis routine is shown in Figure 4. Also included is a method for looking at phase within the particles. The analysis of phase is currently under investigation to determine whether we can extract chemical kinetics from such analysis.

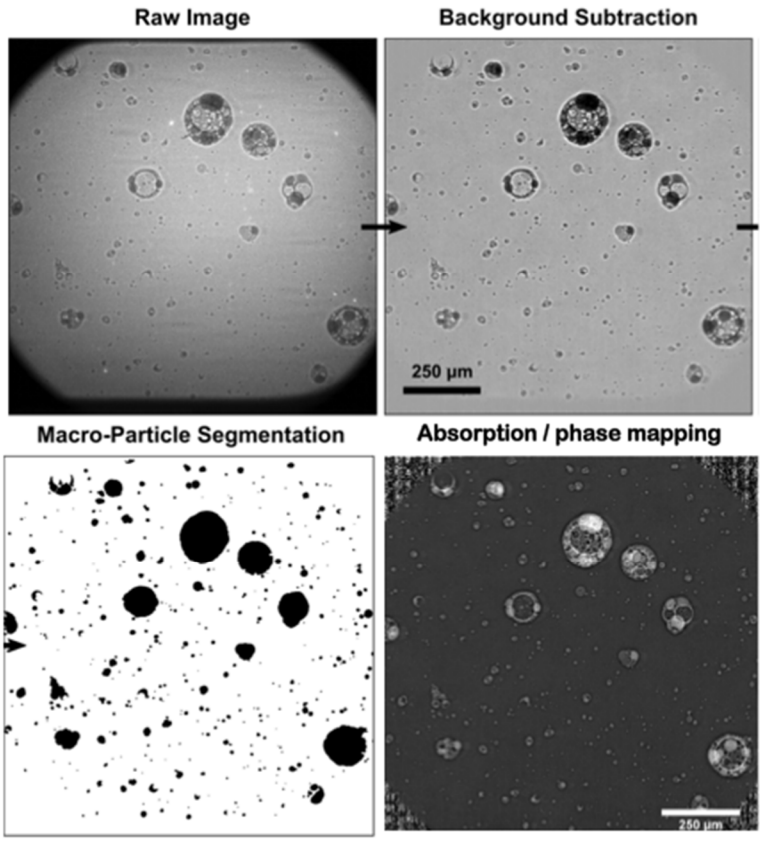

Figure 4: Schematic of the image analysis including background subtraction, particle size analysis, and phase identification.

The average diameter (mass basis) is plotted as a function of time, thermite system, and position of data acquisition in Figure 4. All positions are reported as a percentage of their expansion distance, or x_{end} from Figure 1d. It can be seen that all thermites produce particles at least 10's of microns in size. This is despite the fact that the average primary particle sizes were less than 100 nm in size for all formulations. Between when the particle front arrives (t = 0 ms), and when the particle size plateaus, one can observe a rising slope in particle diameter with time. This rise is sharper at positions closer to the initiation point (1 cm and 25 % data), and rises more slowly at larger expansion distances (75 - 100 %). We believe this rise is due to flow lag; that is, larger particles take longer time to accelerate to a steady state velocity compared to small particles, and so the distance between the fine and coarse particles grows with time.

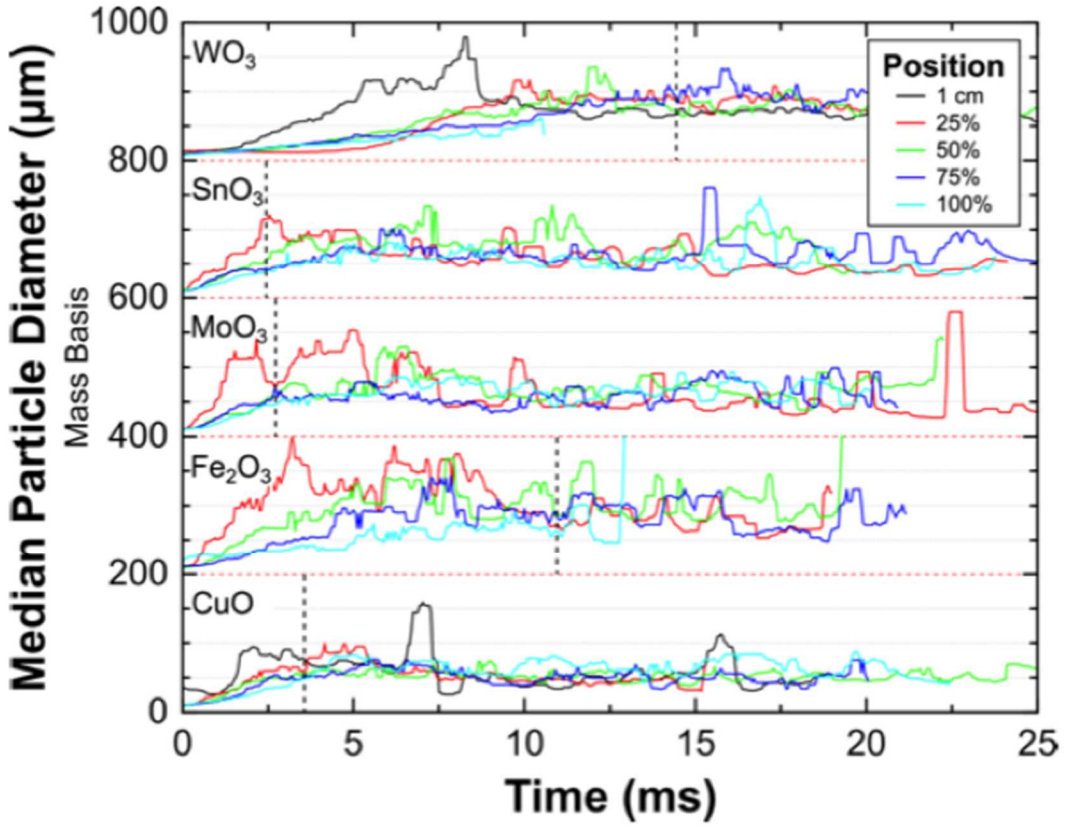

Figure 5: Average particle size as a function of position, time, and oxidizer.

Other observations in this work were that, in all cases, interesting dynamics could be observed within the particles. This included the formation and growth of two-phase particles. The darker phase is assumed to be the molten metal product (Sn, Fe, W, Mo or Cu) as the oxidizer liberates the O2 and proceeds towards the equilibrium phase. The formation and dynamics of this metal product provides some indication of the reaction kinetics, however, further analysis is being performed to verify this. One complication is that one cannot easily distinguish between what is reacting, and what has reacted but not cooled yet. Phase-separation will occur if the materials are immiscible, and if the temperature is hot enough, so decoupling that from chemical kinetics is the major challenge at this point. In any case, these movies have provided significant insight into the size and reaction pathways of thermite reactions.

Impact on Mission

Work on the reaction of thermites has been picked up by campaign 5, and will continue this year. The project is interested in the processing, ignition, and combustion characteristics of these formulations. We have started a collaboration with the New Jersey Institute of Technology to look at milling of custom thermites. Both the Joint Munitions Program and Defense Threat Reduction Agency (DTRA) have funded projects

in FY17 interested in using thermites and other reactive materials as structural energetics. We have hired two postdocs within the materials science division who are, or will be, working with thermites. A third MSD postdoc and a graduate student employed in the materials engineering division have also recently begun looking at 3D printing of thermites. This work is exciting to these young researchers and, unlike some of the 3D printing applications of energetic materials, is highly publishable and presentable. The work was presented as a poster at the Gordon Research Conference, and also at the American Institute of Chemical Engineers meeting in San Francisco. It will be presented at the American Physical Society March meeting in New Orleans, and Dr. Sullivan was invited to give a talk at the APS Shock compression meeting in St. Louis this summer on this work. At least one paper is being finalized for submission within the next couple of months.

Conclusion

This work was very fitting as an LDRD feasibility, and allowed us to collect very high quality movies of deflagrating systems for the first time. We will submit at least one, and possibly two, articles for publications. This work has transitioned to the programs, and will continue there in the near future. While the exact details of the thermite reaction still remain challenging to extract from the movies, the data represents an unprecedented view of the reaction and provides significant insight for future experiments. As part of our future work, we plan to image thermites with different morphologies to see what ultimately controls the unloaded particle size. Phase analysis will also continue, and the goal is to determine whether the absorption coefficient within these particles can be used as a metric of reactivity. If so, this would represent a generic solution for extracting chemical kinetic parameters from composite systems, and would be a highly significant result.

References

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Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.