LLNL-CONF-686343

Nanocomposite Thermite Phenomena at Multiple Length and Time Scales

K. T. Sullivan, A. E. Gash

March 18, 2016

19th International Seminar New Trends in Research of Energetic Materials
Pardubice, Czech Republic
April 20, 2016 through April 22, 2016

Nanocomposite Thermite Phenomena at Multiple Length and Time Scales

Kyle T. Sullivan and Alexander E. Gash

Lawrence Livermore National Laboratory, Livermore, USA

sullivan34@llnl.gov

Abstract:

Using nanoscale constituents in reactive thermite formulations has shown great promise in improving the performance and utility of these materials. Such formulations give rise to rapid liberation of energy in the form of heat and pressure when ignited. Since their discovery, the main method for improving the reactivity has been focused on changing the formulation. In addition to exploring different fuels and oxidizer, a variety of other parameters have been investigated, including particle size and morphology, stoichiometry, density, and degree of confinement. While thermite systems can exhibit strong reactivity scaling with these parameters, it has recently been shown that there are diminishing returns in some cases, such as reducing the particle size of aluminium fuel. To further improve these materials, we must begin to seek alternate methods for changing the reactivity. This requires a detailed understanding of reactive material phenomena occurring at various length and time scales. This understanding would allow us to determine what the major bottlenecks are for achieving rapid reactions, and to come up with alternate solutions for tailoring the reactivity for improved performance. Here we compile recent results on the reaction mechanism occurring in nanocomposite thermites across multiple scales. In all studies, rapid heating experiments are used in order to mimic the dynamic environment in a self-propagating reaction, or the material is combusted and studied in-situ.

Keywords: Thermites; nanocomposite; aluminium; reaction mechanism; 3D printing

1 Introduction

Since 1995, nanoparticles have been investigated as fuels and oxidizers in composite thermite formulations. Aumann et al. first demonstrated that such materials could achieve reactivities nearly three orders of magnitude faster than formulations utilizing larger particles.[1] The main reason for the increased reactivity has been attributed to the reduction in mass transport length scale between the fuel and oxidizer, brought forth when using nanoparticles. This discovery has generated much interest, especially considering that certain formulations have higher mass and volumetric energy densities than even the best explosives. A large focus has been to better understand the governing mechanisms, and explore methods to improve the kinetic time scale, with the hopes of rivaling explosive performance.

Over the years, there have been several important discoveries about the reaction mechanisms in nanocomposite thermites, alternately termed metastable intermolecular composites (MICs). Pantoya et al. have demonstrated that the flame propagation velocity increases as the packing density decreases in confined burn tube tests.[2] This is opposite of what is commonly found for propagating energetic materials. Several authors have found that the forward convection of hot gases is primarily responsible for transporting energy and propagating the flame.[3-5] Some studies have also shown the advection of hot particles can be a mode of heat transfer.[6-8] A variety of oxidizers have been studied and, in general, oxidizers that can rapidly liberate intermediate gases, such as CuO decomposing to release O_2, are found to react faster than those which have more complex decomposition pathways, such as Fe_2O_3.[9] In almost all studies using Al fuel, changing the ratio of fuel to oxidizer can have a large effect on reactivity, and the peak is found to be fuel-rich in most cases. Authors have used thermochemical equilibrium calculations to show that many formulations can produce more gas under fuel-rich conditions and, even though the temperature will be lower than a stoichiometric mixture, this excess gas serves to increase the reactivity by assisting the heat transfer.[4]

Particle size has also been explored, and we have shown diminishing returns of decreasing the size of the fuel, while keeping the size of the oxidizer nanometric.[10] We have hypothesized that there are heat transfer limitations when using small particles, attributed to the time scale of thermal relaxation relative to the intrinsic heating rate generated by the reaction. If the system is unable to react rapidly enough to generate a high gaseous heating rate, then particles will thermally equilibrate with the surrounding gas during the thermal ramp. Thus, for any finite heating rate, there is a critical size below which all particles take equal amounts of time to heat to their ignition point. This can limit energy release rate when using small particles, particularly if the heating time becomes comparable, or slower than, the reaction time scale. In the same work, we demonstrated that larger Al (3.5 µm) outperformed nanometric Al as a fuel.

With diminishing returns being observed, we need to consider alternate methods for tailoring the reactivity of thermites. Before we can achieve this, a deeper fundamental understanding must be developed of what phenomena occur during the reaction, along with what length and time scales dictate these phenomena. Figure 1 illustrates the hierarchy of length scales to consider in the deflagration of a thermite. In the following sections, we will discuss each length scale in further detail.

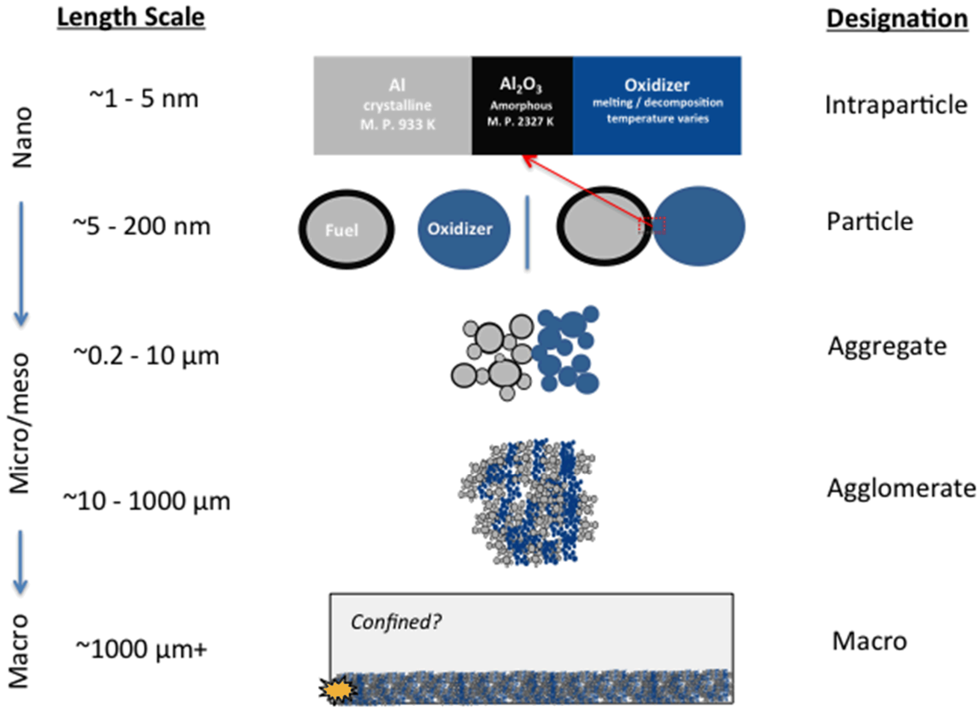

Figure 1: Schematic of the various length scales to consider in the reaction mechanism of nanocomposite thermites.

2 Results and Discussion

2.1 Intraparticle, particle, and aggregate length scales

At the smallest scale of a few nanometers, metal fuel particles have a native amorphous oxide shell passivating the metal core. For aluminum, this shell is only a few nanometers thick, but can represent a significant weight percentage of the particle mass when using nanoparticles. During a rapid thermal ramp, the melting point of the core relative to the melting point of this shell must be considered. If the core melts at a low temperature relative to the shell, such as in the case of Al, this can lead to stresses on the shell as the volume of the core expands during melting. Some authors have hypothesized this to lead to a sudden rupture of the shell, causing the core to unload from the tensile stress.[11-12] This mechanism has been termed the melt dispersion mechanism (MDM), and is said to occur only above a critical heating rate, and only for a range of relative ratios between the shell thickness and particle radius. One major flaw of this mechanism is that it assumes a single spherical particle with a uniform oxide shell. Nanoparticles, including those used to experimentally corroborate this mechanism, are not single particles but are instead aggregates of multiple particles partially sintered with necks adjoining the particles. This will completely change the calculation, as the stress is not isotropic in such a geometry.

A much more plausible explanation of the core-shell interaction is that the oxide shell undergoes softening, phase change, or failure during the thermal ramp, allowing the aluminum core to breach the shell and become accessible to the oxidizer. This process may be assisted by the stresses developed during the melting and volumetric expansion of the core. The coalescence of Al nanoparticle aggregates under rapid heating conditions has been directly imaged using a dynamic transmission electron microscope (DTEM), and the authors showed that particles in aggregates coalesce in as little as 10's of ns once a critical temperature of 1300 K is achieved.[13] An example of this process from reference 13 is shown in Figure 2. It's noteworthy that this temperature is well above the melting point of aluminum, which is where MDM would occur if it were happening. It's impossible to tell the exact mechanism by which the aluminum breaches the oxide shell in these experiments, but knowing a critical temperature and time scale for the coalescence is an important step towards improving our understanding of the dynamic behavior. The results are encouraging in that the mass transport time scale is very fast, 10's of nanoseconds, and so if the oxidizer can be delivered on a comparable time scale, the reaction rate could be very fast as well. However, in many cases this coalescence may have a negative impact in that it greatly reduces the surface to volume ratio of the particles early in the reaction, and before significant oxidation can occur.

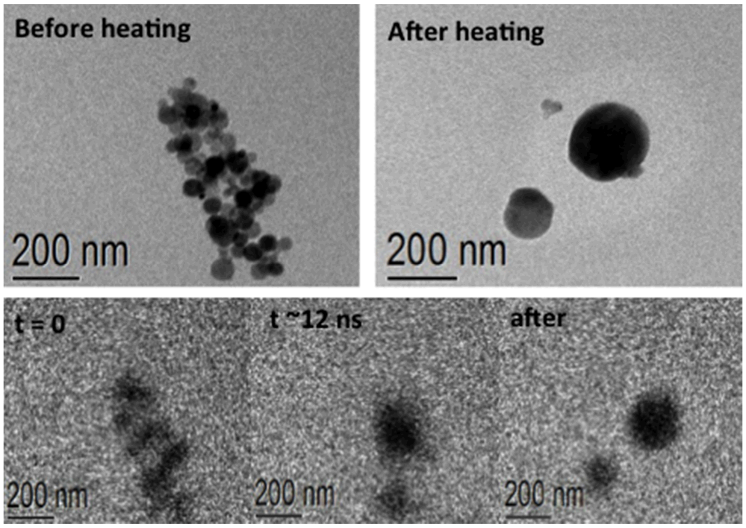

Figure 2: (Top left) Aluminum nanoparticle aggregate before heating. (Top right) Aluminum nanoparticle aggregate coalesced into a sphere, shown after rapid heating. (Bottom) From left to right; before, during, and after images of the coalescence event during rapid heating, taken in pulsed dynamic transmission electron microscope mode. More details can be found in reference 13.

In terms of the oxidizer, particles can undergo a variety of behaviors, including melting, decomposition, and sublimation. Decomposition involves the formation of suboxide species, and this can be a source for the release of oxidizing gases. Thermodynamic calculations, along with thermogravimetric measurements, can both be used to predict the oxide behavior as a function of temperature. However, whether these predictions apply in very rapid heating rate scenarios is uncertain at this point, and would depend on the relative heating time scale relative to the kinetic time scale of phase transformations. Oxidizers will undergo coalescence similar to that seen in the aluminum, and likely on similar time scales. This can serve as a conduit for rapid delivery of the oxidizer to the fuel, however, oxidizing gases may also diffuse and escape before they can react with the fuel in the condensed phase.

The reaction between fuel and oxidizer aggregates has been directly imaged using a rapid-heating hot stage inside a transmission and scanning electron microscope. Both Al / WO_3 [14] and Al / CuO [15] were studied, and were subjected to heating rates of approximately 10^6 K/s. Examples of images before and after heating are shown in Figure 3, and it was observed that the fuel and oxidizer formed an interface and, at least partially, reacted through a condensed-phase pathway. At interfacial locations, the oxidation-reduction reaction creates a hot spot, and this thermal energy is conducted away from the interface and down the aggregate chains. This causes new material to be melted, and surface tension drives the material to flow towards the reacting interface. This mechanism was termed reactive sintering in reference 15, but reactive *coalescence* is a more suitable term in that it includes both sintering and the flow of molten material. It is hypothesized that during this mechanism, the oxidizer can decompose and liberate oxidizing gaseous species. While reactive coalescence is an important part in determining the growth of nanoparticles into larger particles, it is unknown at this time what fraction of the reaction has completed during this event.

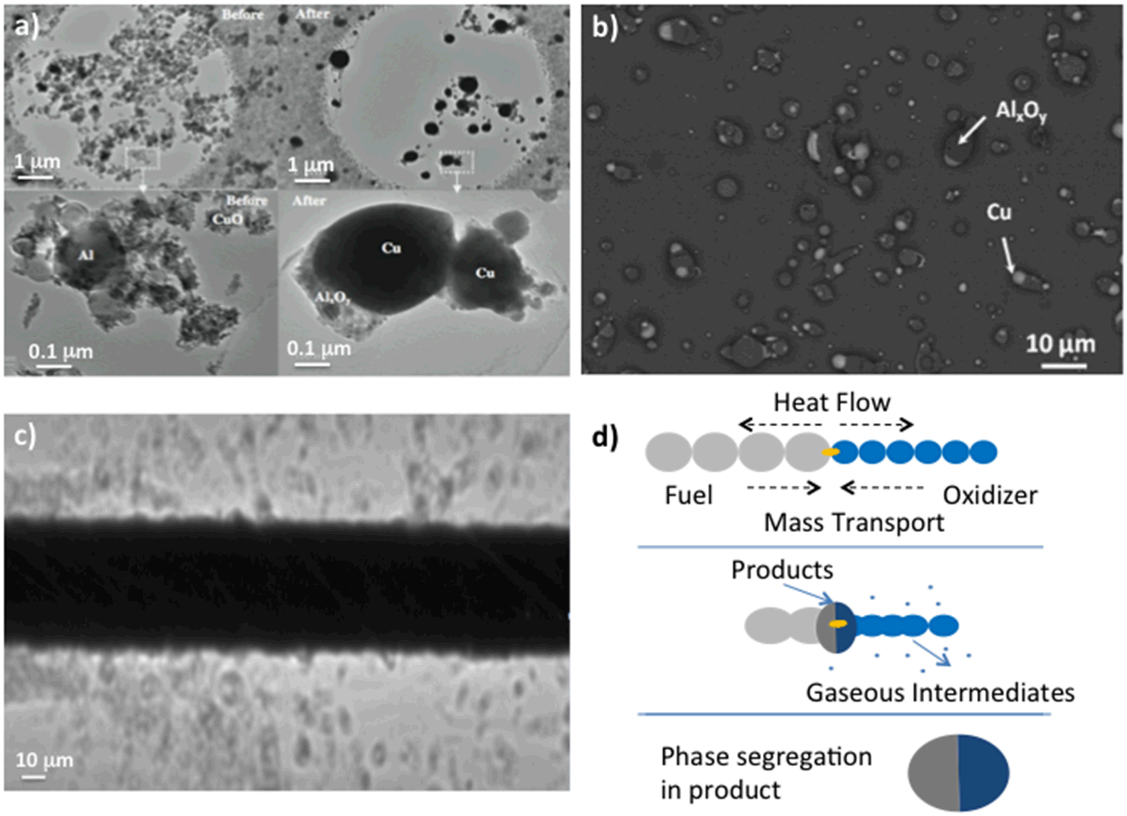

Figure 3: a) Al / CuO thermite before (left) and after (right) rapid heating of 10^6 K/s. Condensed-phase interfacial reactions drive the coalescence of aggregates into micron-scale particles, as seen in reference 15. b) Al / CuO captured at a standoff distance from the reaction, taken from reference 8. The advected particles have a similar morphology as compared to the particles seen in a). c) X-ray phase contrast imaging of reacting Al / CuO on a rapidly heated Pt wire. Coalescence was measured to to occur within a few microseconds after ignition. d) Schematic of reactive sintering, or reactive coalescence, of aggregates to form larger particles. In this mechanism, interfacial reactions drive coalescence of material to flow towards the reacting interface. More details of c) and d) can be found in reference [15].

2.2 Agglomerate length scale

As reactive coalescence occurs, heat and gases are rapidly liberated locally from the aggregates. The behavior at this point is highly dynamic, and involves concurrent melting, coalescence, and outgassing. This interplay between processes sets an additional length scale to consider, which we term the agglomerate length scale, corresponding to a collection of reacting aggregates. To study this length scale, we used electrophoretic deposition to produce films of Al / CuO nanocomposites,[16] and a summary of this work is shown in Figure 4. The thickness of the film was varied from 26-155 µm, and the resultant reactivity and dynamic behavior was investigated using high-speed imaging. It was found that the reactivity could be increased an order of magnitude as the film thickness increased. Furthermore, the behavior exhibited two plateaus in reactivity occurring below and above approximately 40 µm and 110 µm, respectively. Between the plateaus, the reactivity scaling was found to be linear.

By assuming gas buildup and pressure-drive flow in porous media, the time scale for gas escape as a function of film thickness was calculated.[17] This value was compared relative to the known gas production time scale, and a non-dimensional parameter, *A*, was developed. For low values of *A*, which correspond to thin films, liberated gases can escape the film faster than they are produced. For large values of *A*, corresponding to thick films, intermediate gases accumulate faster than they can escape, leading to pressure buildup. This trapping behavior assists the kinetics by keeping the fuel and oxidizer in proximity, and also assists energy transfer by creating internal pressure gradients for the convective transport of energy. However, the pressurized film only persists for a finite amount of time, as the material will undergo unloading and dispersion, if unconfined and a critical stress is reached. Nonetheless, the results were important in demonstrating that at least one other length scale, in this case the film thickness, was important towards controlling the reactivity.

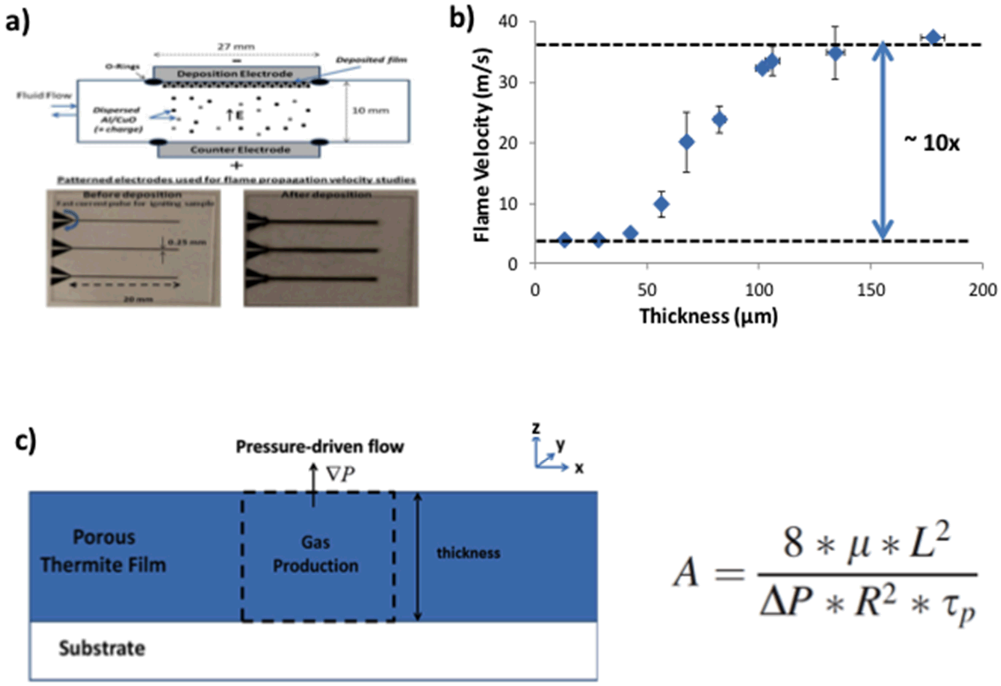

Figure 4: a) Electrophoretic deposition is used to co-deposit Al and CuO nanoparticles onto conductive Pt strips. Film thicknesses range from several microns to nearly 200 microns in this work. b) Linear flame propagation velocity as a function of film thickness. Note the two plateaus, separated by a linear transition regime. More details of a) and b) are in reference [16]. c) Gas trapping parameter, *A*, was calculated assuming pressure-driven flow of intermediate gases out of the porous film. The non-dimensional parameter is a relative ratio of the gas escape to the gas production time scales. For large values of *A*, corresponding to thicker films, gases accumulate and can assist the reaction and energy transport. More details are included in reference [17].

2.3 Macro length scale

At some time scale shortly after gas generation and pressure buildup, the film can undergo pressure-driven unloading, if partially or unconfined. This serves to disperse the gases and, because of the rapid momentum relaxation time scale of small particles, entrains and advects particles in a direction normal to the surface in a multi-phase expansion process. Due to their momentum, coalesced particles can travel large distances relative to the gases. The velocity of these particles has been measured, and was found to be transported 2-3x faster than the flame propagation velocity.[16] If these particles encounter unreacted material, they can assist the energy transport by condensing and igniting material downstream. An example of particle transport and initiation is shown in figure 4.[18] In this case, a thin film of thermite is deposited onto a center strip, along with two neighboring strips. The separation distance tapers down until the strips eventually connect with the center strip. The jump distance, *J*, in which material from the center can be advected sideways and cause sympathetic initiation is quantified. As the *A* parameter is increased, the jump distance was found to increase as well. Thermite films as thin as 100 microns were able to jump at least 9.6 mm, and possibly much further, and ignite neighboring material.

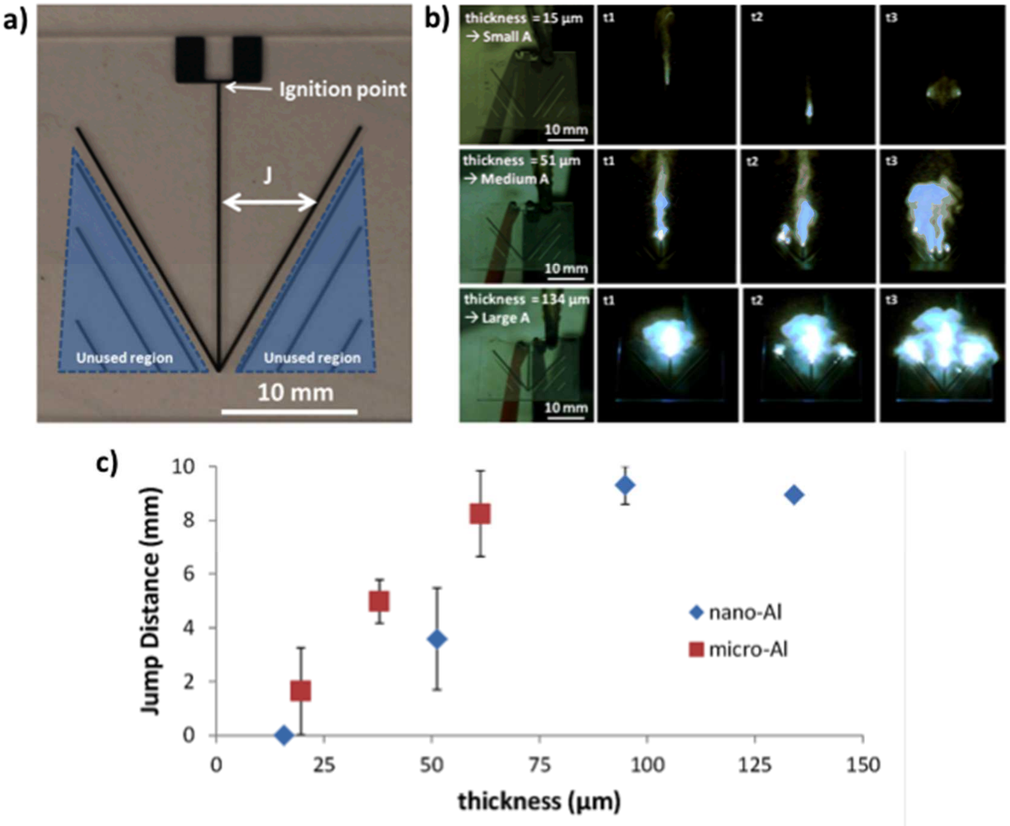

Figure 5: a) Custom electrode, with deposited Al / CuO, designed to measure energy jumping and sympathetic initiation at some distance, *J*. b) Jumping behavior for various values of *A* at different relative times. For large values of *A*, material can jump very large distances and ignite neighbouring material. c) Average jump distance as a function of film thickness for both nanocomposite thermites, as well as thermites using micron-Al. More details can be found in reference [18].

3D printing is a rapidly emerging technology, and is being explored for a very wide range of applications. At the heart of 3D printing is the ability to control, at least down to the micron scale, the spatial placement of material within a part. Thus, with some knowledge of the governing length and time scales, it was conceivable that some of the dynamic processes occurring in nanocomposite thermite reactions could be controlled through engineering the architecture. Doing this required an understanding of the relevant phenomena, along with the ability to print feature sizes commensurate with the length scales governing these phenomena. To create architected thermites, we combined an extrusion-based additive manufacturing technology called direct ink writing (DIW), with electrophoretic deposition of a thermite film.[19] DIW was first used to print 3D electrodes of silver, into two geometries termed channels and hurdles. In a channel, two long parallel strips of silver were oriented parallel to the direction of propagation, and separated by a distance, *d*. In a hurdle geometry, a series of silver barriers were printed perpendicular to the direction of energy propagation, and separated by a distance, *d*. Schematics of these architectures, along with a summary of the results are shown in Figure 6. Al / CuO was deposited conformally onto the surface of the electrodes. As mentioned previously, during pressure unloading a thermite film will undergo a multi-phase expansion, and energy in the form of gases and particles expand in a direction normal to the surface. Thus, the main difference between these two architectures was the orientation of this expansion wave relative to the direction of propagation. The *d-spacing* was varied in each system, and the linear propagation velocity was measured using a high-speed camera.

As can be seen in Figure 6, in the case of channels, the reactivity increases as the *d-spacing* is decreased. This is attributed to the expansion waves overlapping if the channels are situated closely enough. This interaction acts to locally build up pressure, which can increase the forward convective transport of energy. In the case of hurdle geometries, an opposite effect was observed in that the reactivity was seen to increase as the *d-spacing* was increased. The reason for this behavior is a result of the expansion wave being oriented parallel to the direction of propagation. If the *d-spacing* is too low, the multiphase expansion can be physically interrupted as the wave encounters the next hurdle. Furthermore, material from the next hurdle can react and lead to energy pushback, impeding the reaction. However, if the hurdles are situated far enough apart, the expansion wave can fully develop and forwardly advect particles. These particles are intercepted as they encounter the next hurdle and, due to their advection velocity being faster than the baseline velocity, this leads to an increase in the apparent velocity. These results are important in defining other geometric considerations, including the spacing and orientation, which can be used to further control energy release and to tailor the dynamic behavior of such materials. This work opens up the doors for exploring a wide range of architectures, along with scaling the results up to more complex interactions in 3D printed materials.

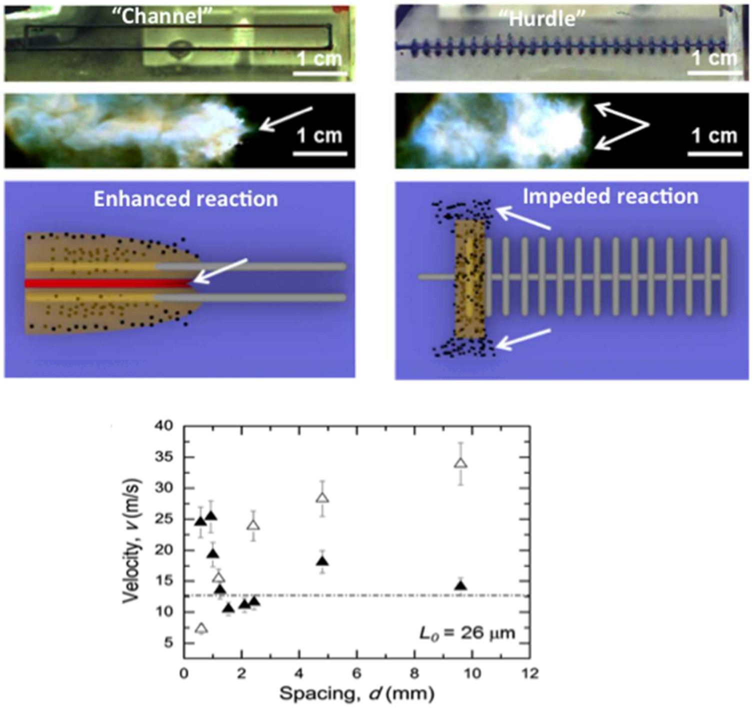

Figure 6: (Left) Channel architecture with a small *d-spacing*, where two expansion waves can overlap in the intermediate region and assist convective energy transport. (Right) Hurdle architecture with a low *d-spacing*, where the expansion wave is intercepted before fully developing. (Bottom) Flame velocity as a function of *d-spacing* for a thin film (L_0 = 26 μm) in the hurdles (open markers) and channel (closed marker) geometries. Note the opposite scaling with the geometric parameter, *d*. The behavior is an artifact of the geometry, as well as the multi-phase expansion the thermite film undergoes upon reaction, and more details are included in reference [19].

3 Conclusions

Here we have compiled several works looking at the mechanistic behavior of nanocomposite thermites across a range of length scales. At high heating rates, nanoparticles are seen to rapidly coalesce and, at least partially, react via interfacial reactions. This creates internal pressurization as gases are released, and the film can undergo unloading as a mixture of gases and particles undergoes a multi-phase expansion. 3D printed can be used to control the energy transport during this event to assist or retard the reactivity. Besides focusing on the mixing scale, this work offers several other length scales and phenomena to consider for further tailoring material reactivity.

Acknowledgments

This work was funded by the Laboratory Directed Research and Development Strategic Initiative Program, 11-SI-004 and 14-SI-005, and performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52–07NA27344. IM release LLNL-CONF-686343.

4 References

[1] C. E. Aumann, G. L. Skofronick, J. A. Martin, Oxidation Behavior of Aluminum Nanopowders, *Journal of Vacuum Science and Technology B,* 13, p. 1178 – 1183, **1995**.

[2] M. L. Pantoya, V. I. Levitas, J. J. Granier, J. B. Henderson, Effect of Bulk Density on Reaction Propagation in Nanothermites and Micron Thermites, *Journal of Propulsion and Power*, 25 (2), p. 465–470, **2009**.

[3] B. S. Bockmon, M. L. Pantoya, S. F. Son, B. W. Asay, J. T. Mang, Combustion Velocities and Propagation Mechanisms of Meta-stable Interstitial Composites, *Journal of Applied Physics*, 98, 064903, p. 1 – 7, **2005**.

[4] V. E. Sanders, B. W. Asay, T. J. Foley, B. C. Tappan, A. N. Pacheco and S. F. Son, Reaction Propagation of Four Nanoscale Energetic Composites (Al/MoO3, Al/WO3, Al/CuO, and Bi2O3), *Journal of Propulsion and Power,* 23 (4), p. 707-714, **2007**.

[5] M. R. Weismiller, J. Y. Malchi, R. A. Yetter and T. J. Foley, Dependence of Flame Propagation on Pressure and Pressurizing Gas for an Al / CuO Nanoscale Thermite, *Proceedings of the Combustion Institute*, 32 (2), p. 1895-1903, **2009**.

[6] S. F. Son, B. W. Asay, T. J. Foley, R. A. Yetter, M. H. Wu and G. A. Risha, Combustion of Nanoscale Al / MoO3 Thermite in Microchannels, *Journal of Propulsion and Power*, 23 (4), p. 715-721, **2007**.

[7] S. W. Dean, M. L. Pantoya, A. E. Gash, S. C. Stacy and L. J. Hope-Weeks, Enhanced Convective Heat Transfer from Non-gas Generating Nanoscale Thermite Reactions, *Journal of Heat Transfer*, 132 □(11), p. 111201, **2010**.

[8] K. T. Sullivan, J. D. Kuntz, A. E. Gash, Electrophoretic Deposition and Mechanistic Studies of Nano-Al / CuO Thermites, *Journal of Applied Physics*, 112, p. 024316, p. 1 – 12, **2012**.

[9] K. Sullivan and M. R. Zachariah, Simultaneous Pressure and Optical Measurements of Nanoaluminum Thermites: Investigating the Reaction Mechanism, *Journal of Propulsion and Power*, 26 (3), p. 467-472, **2010**.

[10] K. T. Sullivan, J. D. Kuntz, A. E. Gash, The Role of Fuel Particle Size on Flame Propagation Velocity in Thermites with a Nanoscale Oxidizer, *Propellants, Explosives, and Pyrotechnics*, 39 (3), p. 407-415, 2014.

[11] V. I. Levitas, Burn Time of Aluminum Nanoparticles: Strong Effect of Heating Rate and Melt-Dispersion Mechanism. *Combustion and Flame*, 156 (2), p. 543-546, **2009**.

[12] V. I. Levitas, B. W. Asay, S. F. Son, and M. Pantoya, Melt Dispersion Mechanism for Fast Reaction of Nano-Thermites, *Journal of Applied Physics*, 89 (7), p. 071909, **2006**.

[13] G. C. Egan, K. T. Sullivan, T. LaGrange, B. W. Reed, and M. R. Zachariah, In Situ Imaging of Ultra-Fast Loss of Nanostructure in Nanoparticle Aggregates. *Journal of Applied Physics*, 115 (8), p. 084903, **2014**.

[14] K. T. Sullivan, W. Chiou, R. Fiore, M. R. Zachariah, In Situ Microscopy of Rapidly Heated Nano-Al and Nano-Al / WO3 Thermites, *Applied Physics Letters*, 97, p. 133104, **2010**.

[15] K. T. Sullivan, N. W. Piekiel, C. Wu, S. Chowdhury, S. T. Kelly, T. C. Hufnagel, K. Fezzaa, M. R. Zachariah, Reactive Sintering: an Important Component in the Combustion of Nanocomposite Thermites, *Combustion and Flame*, 159 (1), p. 2–15, **2012**.

[16] K. T. Sullivan, J. D. Kuntz, and A. E. Gash, Electrophoretic Deposition and Mechanistic Studies of Nano-Al / CuO Thermites, *Journal of Applied Physics*, 112 (2), p. 024316, **2012**.

[17] K. T. Sullivan, S. Bastea, J. D. Kuntz, A. E. Gash, A Pressure Driven Flow Analysis of Gas Trapping Behavior in Nanocomposite Thermites, *Journal of Applied Physics*, 114, p. 164907, **2013**.

[18] K. T. Sullivan, J. D. Kuntz, A. E. Gash, Fine Patterning of Thermites for Mechanistic Studies and Microenergetic Applications, *International Journal of Energetic Materials and Chemical Propulsion*, 12 (6), p. 511-528, **2013**.

[19] K. T. Sullivan, C. Zhu, E. B. Duoss, A. E. Gash, D. B. Kolesky, J. D. Kuntz, J. A. Lewis, C. M. Spadaccini, Controlling Material Reactivity Using Architecture, *Advanced Materials,* 28 (10), p. 1934-1939, **2016**.