Effects of Rheological Properties on Reactivity of Energetic Thin Films

Kelsey A. Meeks^{1,2}, Billy R. Clark¹, Jesus E. Cano¹, Christopher A. Apple², Michelle L. Pantoya^{1*}

¹ Mechanical Engineering Department, Texas Tech University, Lubbock, TX 79409-1021

² Sandia National Labs, Albuquerque, NM 87185 USA

Abstract

Magnesium (Mg) and manganese dioxide (MnO₂) powders were mixed with polyvinylidene fluoride (PVDF) binder and n-methyl pyrrolidone (NMP) solvent and blade cast onto stainless steel foil. The rheological properties of these mixtures were investigated to quantify the mixing condition. Parameters including wet film thickness, equivalence ratio and solids loading were varied. Flame speed and calorific output were investigated for each of these parameters. Results show energy propagation rates increased as a function of dry film thickness, although calorific output remained relatively constant. Stoichiometrically fuel rich compositions were self-quenching, demonstrating the necessity of available oxygen for reaction propagation. A 0.45 solids-liquid mixing ratio resulted in up to an order of magnitude higher energy propagation rate for both open and confined configurations. Rheometry measurements and physical characterizations of the films reveal that the solids loadings resulting in the most stable suspensions also produced the highest energy propagation. Changing solids loading affects the density of the film, which in turn affects energy propagation. Capillary drying forces at high liquid loadings result in higher porosity leading to reduced deposition density and thickness. Very high solids loading results in films with dilatant properties and poor mixing. These results show solids loading affects mixing and energy propagation and could impact slurry cast energetic materials as in additive manufacturing processes.

* Corresponding Author Contact Information: Email: michelle.pantoya@ttu.edu; Phone: 806-834-3733

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Introduction

The processes of joining, brazing, and welding have been around for over 100 years, but the demands of miniaturization and integration of multiple disparate materials is placing new demands on the field, requiring new solutions to making small, precision joinings that are mechanically, thermally, and hermetically robust. In many of these cases, the traditional methods of externally applied heat to drive the reactions simply cannot be employed, due to reactivity or temperature sensitivity of one or more of the joining components (such as the batteries or electronics). New methods for precision application of heat at the point of joining must be developed. One possible method involves the use of energetic materials embedded into the joint to supply a precise amount of heat over a controlled time to drive the joining process locally without transmitting heat globally. To meet these kinds of demands, strongly localized exothermic reactions that can be patterned, deposited and locally applied become necessary.

Thermite reactions are ideal for this application because they produce highly localized and intense heat [1], [2]. Thermite is defined here as consisting of a metal fuel combined with a metal oxide and may include a binder. These reactions are characterized by self-sustained propagation, high temperatures and high heats of combustion, and have been developed for use as heat sources for many applications such as welding and joining [3]. Reaction rate for thermites is dependent on a number of factors including equivalence ratio, dilution with the inert product, temperature, compaction density and particle diameter [4]. Although experimental

study often focuses on loose powders, a binder is necessary for many applications requiring the consolidation of energetic powders into compacts or coatings necessary to make robust films capable of withstanding processing until the time is appropriate for reaction. Thus, binders such as polyvinylidene fluoride (PVDF), Viton® fluoroelastomer (Viton) [5] and paraffin [6] have been implemented. These binders can also improve mechanical properties of formulations [7].

For many thermites, equivalence ratio has been shown to have a significant influence on flame speed. Many works have shown thermites burn more effectively when the equivalence ratio is slightly fuel rich [8]. Son et al. showed that the highest flame speed coincided with slightly fuel rich stoichiometries and also corresponded to the highest gas generation [9]. However, low gas generating thermite composites have a different thermal transport mechanism; namely, by hot particle advection or conductive heat transfer [10], such that changing stoichiometry may not have the same significant influence on flame speed. In fact, Armstrong [11] modeled flame speeds through random particulate media with the assumption of no gas generation and showed thermal properties of the matrix are key parameters controlling flame speed given second order Arrhenius reaction kinetics for a global reaction.

Many processes exist for the preparation of thermite thin films, including electrophoretic deposition [12], sol-gel synthesis [13], physical vapor deposition [14] and cold spraying [15]. Recently, blade casting was added to this list and implemented as a deposition method for thermites [16]. Blade casting is a method for deposition of a colloid using a blade with a set gap width [16]. The approach involves combining the base thermite (i.e., fuel and oxidizer particles) with a binder and solvent system to create a slurry that is then deposited on a substrate using a blade (e.g., sometimes referred to as doctor blading). This process is also a first step in additive manufacturing of energetic materials that require extrusion of a colloid energetic mixture.

By selecting blades with different gap widths, the thickness of blade cast films can easily be altered. Thickness of the thermite coating has been shown to have an effect on combustion [17]. Sullivan et al. [18] showed a correlation between film thickness and flame speed for electrophoretically deposited thin films. Namely, as the thickness of the film increased, flame speed also increased. This relationship is asymptotic at the ends, and approaches a set value at critical high and low thicknesses. It was postulated that this transition was due to a shift in propagation mechanism from convection to advection, or that convective transport was enhanced by the trapping of more gasses [18].

Blade casting has been used extensively in the preparation of ceramic thin films, for applications including battery manufacture [19]. For this approach, solids loading by mass in the slurry plays a large role in the morphology of the deposited film and on the final deposition density. For thermites, density has been shown to have an impact on flame speed [20],[21],[22],[23], and recently it was shown that solids loading during resonant mixing affected burn properties of Al-Bi₂O₃ nanopowders, with high or low solids loadings resulting in reduced combustion performance [24]. In ceramic thin films, higher solids loading has been shown to result in less settling, less deposition shrinkage during drying, and results in denser, less porous films [25]. However, at very high solids loading the resultant suspension has dilatant properties leading to low quality films [26]. The findings from ceramic thin films research have relevance to thermites whose reaction behavior can vary with mixture homogeneity, deposition thickness, density and porosity.

The objective of this work is to establish blade casting as an effective approach for synthesizing thermite films by examining mixing parameters that impact the resultant

depositions. In particular, viscosity of the slurry and its influence on deposition homogeneity will be investigated. Another objective is to characterize the energetic nature of the newly synthesized films. Towards this end, two parameters are measured: flame speed and calorific output. These measurements are coupled with thermal equilibrium simulations to assess variations in heat of combustion, gas generation and adiabatic flame temperature. This experimental characterization, coupled with simulations, provides insight to the reactive nature of the thermite films. To accomplish these objectives, thin films of magnesium (Mg) and manganese dioxide (MnO_2) were synthesized using a polyvinylidene fluoride (PVDF) binder dissolved in n-methyl-pyrrolidone (NMP). This is a relatively high heat but non-gas generating mixture purposefully selected for application of heat at the point of joining.

Experimental Procedure

Materials and Synthesis

Powdered magnesium (Mg) with a purity of 99.8% and manganese dioxide (MnO_2) with a purity of 99.95% were obtained from Alfa Aesar as micron sized particles sieved to a -325 mesh. These powders were mixed to the desired stoichiometric ratio with polyvinylidene fluoride (PVDF) which had been dissolved in n-methyl-pyrrolidone (NMP). Both Mg and MnO_2 particles have an amorphous structure. Average Mg particle diameter is $30\mu\text{m}$, and average MnO_2 particle diameter is $5\mu\text{m}$. The PVDF-NMP solution was added in concentrations so that the final loading of PVDF in the dry film was 1% by mass. Excess solvent was added to reach the desired solids loading by volume in the liquid mixture. For varying wet film thickness and equivalence ratio, the slurry was mixed in a planetary centrifugal mixer (AR250, Thinky, Japan) at 1200RPM for four minutes. The mixture was then blade cast using a $200\mu\text{m}$ draw down blade

onto 50 μm stainless steel foil using an Elcometer 4340 (Elcometer, UK). The blade cast apparatus is illustrated and described in detail in [16]. Samples were dried in a fume hood for several hours, and then baked in a vacuum oven at 333K for at least 6 hours. The substrate was then cut into smaller samples, and deposition thickness was measured using a Starrett Electronic Indicator (Starrett, Athol, MA).

Experimental Measurements: Flame Speed

Since it is necessary to determine both the total energy released during the reaction and rate of energy release to the localized region, calorimetry data was coupled with flame speed measurements. It is expected that the incorporation of a binder will impact the rates of energy release, due to either the pyrolysis in situ of the binder chemistry, or the suppression of transport for the thermite reaction that would drive energy propagation down depending on how the reactant species are transported at the flame front in the presence of the binder. Samples were cut into strips measuring approximately 60mm by 6mm for flame speed tests and affixed to a glass slide using a non-conductive adhesive, then placed in the combustion chamber and positioned perpendicular to the viewing window. The chamber was evacuated and backfilled with argon twice to achieve an inert environment at 67 kPa pressure. Ignition was achieved using a small gage tungsten hot wire, and the reaction recorded by a high speed Photron Fastcam camera. Post-processing of the recording to determine flame speed was completed in Labview Vision Builder 2010.

For varying solids loading, flame speed measurements were also taken in confinement. For this set of experiments, the slurry was mixed in a planetary centrifugal mixer at 1600 RPM for one and a half minutes. The rotational rate was increased to achieve sufficient mixing at higher solids loadings, and the mixing time was decreased to avoid overheating the mixer.

Viscosity of the resultant suspension was measured using a viscometer (Brookfield). The slurry was cast using a 160 μm draw-down blade onto 50 μm stainless steel foil. Draw-down blade thickness was decreased so that samples could easily fit into the confinement apparatus. Samples were immediately baked in the vacuum oven and when dried, the coated foils were cut into smaller samples and deposition thickness measurements were taken.

Confined flame speed was measured using a confinement apparatus shown in Figure 1. Many applications consist of films in a confined configuration, such that this analysis has relevance to engineering of the thermite film technology. To assemble the confinement apparatus, a 63 x 27 x 5 mm groove was cut into a 102 x 76 mm acrylic block. Another 102 x 76 mm acrylic block was fastened on top of the first block with bolts at each of the four corners. Samples were placed in the confinement apparatus with approximately 5 mm exposed in order to prevent the tungsten hot wire used for ignition from melting the acrylic. Flame speeds were recorded using a Phantom high speed camera and post-processed in Labview Vision Builder 2010.

Experimental Measurements: Heat of Combustion

Heat of combustion measurements were collected in a bomb calorimeter (Parr 6200 Calorimeter). The sample chamber was pumped and purged with argon twice prior to firing, then placed in a water bath. Samples were initiated using resistance heating by a thin gage tungsten wire. The temperature rise of the water bath was recorded and used to calculate the resultant heat of combustion. Heat of combustion calculations were performed in accordance with the ASTM standard [27].

Thermochemical Equilibrium Simulations

To further understand combustion properties, simulations were performed using thermal-chemical equilibrium software, REAL (Timetec L.L.C). The heat of combustion was calculated for a mixture of Mg and MnO₂ with varying equivalence ratios. Each simulation included one percent added PVDF by mass, to more accurately capture the predicted behavior of the experimental thin films. Simulations were run assuming a constant volume of 0.01 m³/kg and internal energy equal to zero kJ/kg. The adiabatic flame temperature was calculated assuming a constant pressure of 101,325 Pa and an enthalpy equal to zero kJ/kg. These calculated values of heat of combustion and adiabatic flame temperature are an upper limit for the ideal case of complete combustion. Previous work using this software showed good agreement between simulated and measured adiabatic flame temperature [1], [2].

Results and Discussion

Deposition Characteristics

Dry film thickness and sample mass measurements were taken for all depositions. From these, deposition density and percentage of the theoretical maximum density (TMD) were calculated. These measurements and calculations are shown in Table 1. Note that as wet film thickness increases, so does dry film thickness and deposition density. As equivalence ratio increases, the dry film thickness increases, possibly due to the change in mixing properties of Mg and MnO₂ that are affected by their differing particle morphologies. Shrinkage of sol-gel films has been shown to be a function of porosity, with low liquid loadings leading to high capillary forces which collapse the film structure and produce denser films [28], [29]. The same trend is apparent in these films, as dry film thickness increases with solids loading, and deposition density is highest for high solids loadings. The standard deviations reported in Table 1 are from

repeatability of six test samples and represent the highest uncertainty in the data. It is interesting to note that denser coatings have less variability and smaller standard deviations.

Additionally, a sample was sectioned and examined using a SEM to better analyze deposition characteristics. The sample depicted in Fig. 2 is from a deposition with 40% solids by volume loading, a wet film thickness of 203 microns and stoichiometric equivalence ratio. Figure 2 depicts this cross section of the coating, with the substrate just below the bottom of the image. The image in the top left is a backscatter image of the sample, the bottom images are Energy Dispersive Spectroscopy (EDS) images showing occurrences of Mg and Mn, and the top left image is a composite image of these three images. Note that the material appears homogeneous and well mixed with no appreciable settling. Also note that in general, the Mg particles are larger than the Mn particles.

Dry Film Thickness

Figure 3 shows the flame speed as a function of dry film thickness. Each point on the graph represents an average of six flame speed tests. Each sample was mixed to a solids concentration of 40% by volume, an equivalence ratio of 1 for the Mg-MnO₂ reactants, and cast using a 200 micron drawdown blade onto 50 micron stainless steel foil. All tests were performed in an argon environment. For this range of thicknesses, flame speed increased from an average of 95 to 110 cm/s as a result of increasing thickness from 100 to 225 microns. While the range of measured flame speed varies by as much as 18% in some cases, all of these depositions result in energy propagation consistently on the order of 100 cm/s and confirm blade casting as a viable approach for synthesizing thermite films.

Heat of combustion measurements reported are averages of six tests with repeatability being the largest source of uncertainty at 1%. Figure 4 shows calorific output for all samples are roughly equivalent. This indicates that changing film thickness does not greatly alter the degree of particle mixing to impact overall calorific output. Although flame speed does increase with increasing dry film thickness (Fig. 4), an increase in dry film thickness of near 115% results in only a 15% increase in flame speed. The sensitivity of highly gas generating thermite composites to flame thickness has been reported [18], and low gas generating thermites, such as Mg-MnO₂, appears comparatively insensitive to changes in film thickness over a similar range of thickness. It is notable that although flame speed increases with increasing dry film thickness (Fig. 3), the heat of combustion does not (Fig. 4). That is, thicker films demonstrate higher flame speeds, but not more chemical energy per unit mass. This implies that energy transport rather than chemical energy liberated from the reaction plays a more dominant role in raising the flame speed for thicker films.

Equivalence ratio

It has been shown that many thermites produce the highest flame speeds slightly fuel rich [8]. In order to determine the effect of equivalence ratio on flame speed and calorific output, samples were prepared at equivalence ratios ranging from 0.9 to 1.4 (i.e., fuel lean to fuel rich; stoichiometric has an equivalence ratio of unity). Measurements of flame speed and calorific output as a function of equivalence ratio are shown in Table 2. Samples prepared at the fuel rich stoichiometries of 1.2 and 1.4 did not sustain propagation. This is possibly due to the combustion occurring in argon, where no excess oxygen is available to facilitate combustion.

Figure 5 shows the measured heat of combustion, as well as the calculated heat of combustion and adiabatic flame temperature data for simulations performed using thermochemical equilibrium software. Combustion was simulated in an inert (no excess oxygen) environment. The simulated heat of combustion values show similar trends to the measured values, with the heat of combustion highest near stoichiometric. The simulated heats of combustion are higher than measured values, which is expected since the simulation assumes complete combustion.

In Fig. 5, adiabatic flame temperature decreases as equivalence ratio increases, dropping close to 2000K for an equivalence ratio of 1.4, making the flame unlikely to self-propagate. A strong indication that a reaction is self-propagating is an adiabatic flame temperature greater than 2000K [30], [31]. Another indication that a reaction will be self-propagating is if at least one of its product species is brought to its melt temperature [32]. These may be contributing factors to the films prepared at equivalence ratios of 1.2 and 1.4 quenching, unable to sustain energy propagation. It is also interesting to note that flame speed correlates well with the simulated adiabatic flame temperature. The adiabatic flame temperature decreases as equivalence ratio increases (Fig. 5), and the flame speed decreases as equivalence ratio increases to zero (self-quenching) at equivalence ratios above one (Table 2). This is an indication that conductive energy from high reaction temperatures is facilitating energy propagation and is the dominant energy transfer mechanism.

Although many thermites burn faster slightly fuel rich, this does not appear to be the case for these composites. Many of the experiments showing a correlation between fuel rich stoichiometries and higher flame speeds were performed in ambient air or high oxygen environments where excess oxygen was available to participate in the reaction [33]. The tests

conducted in this study were performed in argon, with no excess oxygen available. The heats of combustion recorded are highest near stoichiometric and decrease as the equivalence ratio diverges and simulations support this trend. The lack of self propagation observed at high equivalence ratios also suggests the importance of sufficient oxygen availability during reaction, indicating that in oxygen poor environments, the benefit of excess fuel to improved combustion performance is greatly reduced, if not eliminated.

Solids Loading

Rheology measurements of the solutions prior to casting are shown in Fig. 6, with viscosity of the solids measured in centipoise (cP) shown on a log-log scale. For low shear rates, the higher solids loading solutions have higher viscosities. However, as the shear rate increases, the viscosity disparity decreases. For high solids loadings, the very high viscosities at low shear rates indicate suspensions with poor liquidity. In contrast, suspensions with low solids loadings are rheologically thin and will display low viscosities at both low and high shear rates. All of these coatings exhibit shear thinning behavior, however, the ideal coating rheology would have comparatively low viscosity for low shear rates, but would retain a high viscosity at higher shear rates, exhibiting less shear thinning (or more dilatant behavior). Based on this criterion and the above data, a solids loading of 45 or 47% would provide the optimum balance of relatively low viscosity for low shear rates coupled with higher viscosity at higher shear rates (Fig.6).

The flame speed for both the open and confined configurations are shown in Fig. 7. Flame speed increases from 43 to 45 % solids and then decreases after this point. From rheological theory, it is known that there is an ideal solids loading at which colloid materials will achieve the highest degree of dispersion in the solvent [34], [35]. At solids loadings below this point, the solution will be thin and particle settling will occur. Above this point, the solution is

too viscous, causing particles to jam against one another during flow and inhibit mixing. The exact location of this point is highly dependent on particle size and morphology. In Fig. 7 the highest flame speeds for the Mg-MnO₂-PVDF-NMP solution occurred at a solids loading of 45%, which is consistent with the rheological optimum observed during viscosity testing. Both confined and unconfined flame speeds demonstrate this behavior, although the confined flame speeds are an order of magnitude higher than the unconfined. This is probably due to the directionalization of the advected particle cloud, as observed in previous work [16]. These results demonstrate a high degree of repeatability due to the consistent confinement provided by this diagnostic approach. Overall the ideal mixing condition of 45% solids loading shows optimum rheology properties as well as highest flame speed. These results indicate that rheology properties during mixing for blade cast formulations are critically important to the combustion performance as quantified by the order of magnitude variation in flame speed (Fig. 7).

Conclusions

Thin film energetic composites composed of Mg-MnO₂-PVDF were blade cast with varying parameters of film thickness, stoichiometry and solids loading. These parameters influence rheology and are important in deposition as well as combustion. As wet film thickness increases from 200 to 500 microns, flame speed increases up to 110 cm/s, yet negligible variation in calorific output was observed for variations in film thickness.

In an argon environment, Mg-MnO₂-PVDF at stoichiometric equivalence will sustain propagation, but fuel rich mixtures are self-quenching. This behavior demonstrates the importance of sufficient available oxygen for reaction propagation.

The rheology properties for a volumetric solids loading of 45% is ideal for producing the highest flame speeds. Higher volumetric solids loading results in compositions with poor liquidity and slower flame speeds. Lower volumetric solids loadings result in rheologically thin suspensions that may lead to settling or more porous structure in the dried film. More generally, it was found that there exists an ideal solids ratio for mixing and that higher or lower loadings adversely affect mixing resulting in reduced flame speeds. It is therefore very important to carefully select mixing parameters to maximize reaction efficiency.

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References

- [1] K. Kappagantula, C. Crane, and M. Pantoya, "Determination of the spatial temperature distribution from combustion products: a diagnostic study.," *Review of Scientific Instruments*, vol. 84, no. 10, p. 104902, Oct. 2013.
- [2] M. . Kappagantula, K., Crane, C., Pantoya, "Factors Influencing Temperature Fields During Combustion Reactions," *Propellants, Explosives, Pyrotechnics*, vol. 39, no. 3, pp. 434–443, 2014.

- [3] J. Wang, E. Besnoin, A. Duckham, S. J. Spey, M. E. Reiss, O. M. Knio, M. Powers, M. Whitener, and T. P. Weihs, "Room-temperature soldering with nanostructured foils," *Applied Physics Letters*, vol. 83, no. 19, p. 3987, 2003.
- [4] A. Kanury, "A kinetic model for metal+ nonmetal reactions," *Metallurgical Transactions A*, vol. 23, no. September, pp. 2349–2356, 1992.
- [5] C. D. Yarrington, S. F. Son, and T. J. Foley, "Combustion of Silicon/Teflon/Viton and Aluminum/Teflon/Viton Energetic Composites," *Journal of Propulsion and Power*, vol. 26, no. 4, pp. 734–743, Jul. 2010.
- [6] A. Al-Harathi and A. Williams, "Effect of fuel binder and oxidiser particle diameter on the combustion of ammonium perchlorate based propellants," *Fuel*, vol. 77, no. 13, pp. 1451–1468, Oct. 1998.
- [7] R. H. B. Bouma, D. Meuken, R. Verbeek, M. Martinez Pacheco, and L. Katgerman, "Shear Initiation of Al/MoO₃-Based Reactive Materials," *Propellants, Explosives, Pyrotechnics*, vol. 32, no. 6, pp. 447–453, Dec. 2007.
- [8] G. M. Dutro, R. a. Yetter, G. a. Risha, and S. F. Son, "The effect of stoichiometry on the combustion behavior of a nanoscale Al/MoO₃ thermite," *Proceedings of the Combustion Institute*, vol. 32, no. 2, pp. 1921–1928, 2009.
- [9] 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*, vol. 23, no. 4, pp. 715–721, Jul. 2007.
- [10] V. Sanin, S. Silyakov, and V. Yuxhvid, "Propagation of a burn front through a long channel," *Combustion, Explosion and Shock ...*, vol. 27, no. 4, pp. 674–677, 1991.
- [11] R. Armstrong, "Models For Gasless Combustion in Layered Materials and Random Media," *Combustion and Science Technology*, vol. 71, pp. 155–174, 1990.
- [12] A. J. Pascall, K. T. Sullivan, and J. D. Kuntz, "Morphology of electrophoretically deposited films on electrode strips.," *The journal of physical chemistry. B*, vol. 117, no. 6, pp. 1702–7, Feb. 2013.
- [13] O. Cervantes, J. Kuntz, A. Gash, and Z. Munir, "Heat of combustion of tantalum–tungsten oxide thermite composites," *Combustion and Flame*, vol. 157, no. 12, pp. 2326–2332, 2010.
- [14] C. Lanthony, J.-M. Ducr, A. Estve, C. Rossi, and M. Djafari-Rouhani, "Formation of Al/CuO bilayer films: Basic mechanisms through density functional theory calculations," *Thin Solid Films*, vol. 520, no. 14, pp. 4768–4771, May 2012.
- [15] A. Bacciochini, M. I. Radulescu, Y. Charron-Tousignant, J. Van Dyke, M. Nganbe, M. Yandouzi, J. J. Lee, and B. Jodoin, "Enhanced reactivity of mechanically-activated nano-

- scale gasless reactive materials consolidated by coldspray,” *Surface and Coatings Technology*, vol. 206, no. 21, pp. 4343–4348, Jun. 2012.
- [16] K. Meeks, M. L. Pantoya, and C. Apblett, “Deposition and characterization of energetic thin films,” *Combustion and Flame*, Nov. 2013.
 - [17] D. M. Ikornikov, V. N. Sanin, and V. I. Yuxhvid, “Combustion of thermite systems in thin layers with an open surface,” *Combustion, Explosion, and Shock Waves*, vol. 47, no. 6, pp. 697–702, Dec. 2011.
 - [18] K. T. Sullivan, J. D. Kuntz, and a. E. Gash, “Electrophoretic deposition and mechanistic studies of nano-Al/CuO thermites,” *Journal of Applied Physics*, vol. 112, no. 2, p. 024316, 2012.
 - [19] E. Vidal, J. M. Rojo, M. C. García-Alegre, D. Guinea, E. Soto, and J. M. Amarilla, “Effect of composition, sonication and pressure on the rate capability of 5V-LiNi_{0.5}Mn_{1.5}O₄ composite cathodes,” *Electrochimica Acta*, vol. 108, pp. 175–181, Oct. 2013.
 - [20] M. L. Pantoya, V. I. Levitas, J. J. Granier, and J. B. Henderson, “Effect of Bulk Density on Reaction Propagation in Nanothermites and Micron Thermites,” *Journal of Propulsion and Power*, vol. 25, no. 2, pp. 465–470, Mar. 2009.
 - [21] E. M. Hunt and M. L. Pantoya, “Impact sensitivity of intermetallic nanocomposites: A study on compositional and bulk density,” *Intermetallics*, vol. 18, no. 8, pp. 1612–1616, Aug. 2010.
 - [22] M. Pantoya and J. Granier, “Combustion Behavior of Highly Energetic Thermites: Nano versus Micron Composites,” *Propellants, Explosives, Pyrotechnics*, vol. 30, no. 1, pp. 53–62, Feb. 2005.
 - [23] 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*, vol. 23, no. 4, pp. 707–714, Jul. 2007.
 - [24] R. R. Nellums, B. C. Terry, B. C. Tappan, S. F. Son, and L. J. Groven, “Effect of Solids Loading on Resonant Mixed Al-Bi₂O₃ Nanothermite Powders,” *Propellants, Explosives, Pyrotechnics*, vol. 38, no. 5, pp. 605–610, Oct. 2013.
 - [25] M. Liu, H. Zhou, H. Zhu, Z. Yue, and J. Zhao, “Tape casting of borosilicate glass/Al₂O₃ composites for LTCC substrate with various relative molecular masses of PVB,” *Journal of Central South University*, vol. 20, no. 1, pp. 37–43, Jan. 2013.
 - [26] G. Jian, D. Zhou, J. Yang, and Q. Fu, “Tape casting of cobalt ferrite from nonaqueous slurry,” *Journal of Magnetism and Magnetic Materials*, vol. 324, no. 24, pp. 4179–4183, Dec. 2012.

- [27] ASTM International, "Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method)," 2013.
- [28] A. Soleimani Dorcheh and M. H. Abbasi, "Silica aerogel; synthesis, properties and characterization," *Journal of Materials Processing Technology*, vol. 199, no. 1–3, pp. 10–26, Apr. 2008.
- [29] H. Omranpour, A. Dourbash, and S. Motahari, "Mechanical properties improvement of silica aerogel through aging: Role of solvent type, time and temperature," *American Institute of Physics Conference Proceedings*, vol. 298, pp. 298–302, 2014.
- [30] L. . Wang, Z. A. Munir, and Y. M. Maximov, "Thermite reactions: their utilization in the synthesis and processing of materials," *Journal of Materials Science*, vol. 28, no. 14, pp. 3693–3708, 1993.
- [31] J. Moore and H. Feng, "Combustion synthesis of advanced materials: Part I. Reaction parameters," *Progress in Materials Science*, vol. 39, no. 94, pp. 243–273, 1995.
- [32] A. Hardt and P. Phung, "Propagation of gasless reactions in solids—I. Analytical study of exothermic intermetallic reaction rates," *Combustion and Flame*, vol. 21, pp. 77–89, 1973.
- [33] C. W. Farley, M. L. Pantoya, and V. I. Levitas, "A mechanistic perspective of atmospheric oxygen sensitivity on composite energetic material reactions," *Combustion and Flame*, vol. 161, no. 4, pp. 1131–1134, Apr. 2014.
- [34] A. Goswami, A. K. N. Balashanmugam, A. M. Umarji, and G. Madras, "Optimization of rheological properties of photopolymerizable alumina suspensions for ceramic microstereolithography," *Ceramics International*, vol. 40, no. 2, pp. 3655–3665, Mar. 2014.
- [35] M. Vicent, E. Sánchez, G. Mallol, and R. Moreno, "Study of colloidal behaviour and rheology of Al₂O₃–TiO₂ nanosuspensions to obtain free-flowing spray-dried granules for atmospheric plasma spraying," *Ceramics International*, vol. 39, no. 7, pp. 8103–8111, Sep. 2013.

Figure Captions

Figure 1. Confinement apparatus used for confined flame speed tests. Exploded view with dimensions.

Figure 2. SEM and EDS image of cross section of deposition with 40% solids, 203 micron wet film thickness and an equivalence ration of 1. Distribution of Mg-MnO₂ is consistent with well mixed deposition and shows no evidence of settling.

Figure 3. Flame speed as a function of dry film thickness. Flame speed increases as a function of increasing dry film thickness.

Figure 4. Calorific output as a function of dry film thickness. As dry film thickness increases, calorific output remains relatively constant.

Figure 5. Measured heat of combustion, as well as simulated heat of combustion and adiabatic flame temperature in REAL. Heat of combustion is highest at stoichiometric equivalence for the measured and simulated values. Simulated adiabatic flame temperature decreases with increasing equivalence ratio.

Figure 6. Viscosity of suspensions for different solids contents. Higher solids loadings result in higher viscosities, particularly at low shear rates.

Figure 7. Unconfined (open) and confined flame speed as a result of changing volumetric solids content. Flame speeds are higher for the confined burns than for the unconfined. For both configurations, flame speed is highest for a volumetric solids content of 45%, and decreases with increasing deviation from this ideal point.

Table 1 Dry film thickness and deposition density for different magnesium-manganese dioxide Coatings.

		Dry Film Thickness (microns)	Standard Deviation of Thickness	Percent Shrinkage	Deposition Density (g/cm ³)	Standard Deviation of Density	Percent TMD
Wet Film Thickness (microns)	203	100	7.11	50.9%	1.34	0.21	45.1%
	254	127	5.83	49.9%	1.58	0.13	53.6%
	381	181	9.90	52.4%	1.64	0.05	55.3%
	508	229	7.00	55.0%	1.66	0.05	55.6%
Equivalence Ratio	0.9	86	5.11	57.7%	1.80	0.09	59.0%
	1.0	98	6.49	51.7%	1.34	0.21	45.1%
	1.2	100	7.33	50.6%	1.57	0.11	55.2%
	1.4	103	6.77	49.4%	1.33	0.05	48.6%
Solids Content	43	57	2.04	52.5%	1.25	0.16	41.8%
	45	64	1.79	46.7%	1.35	0.09	45.1%
	47	70	1.52	41.7%	1.36	0.24	45.5%
	49	80	1.54	33.3%	1.33	0.04	44.5%

Table 2 Flame speed and heat of combustion for varying equivalence ratio

Equivalence Ratio	Flame Speed (cm/s)	Flame Speed Standard Deviation	Heat of Combustion (kJ/g)	Heat of Combustion Standard Deviation
0.9	94.52	7.09	3.81	0.07
1	71.55	1.39	3.93	0.22
1.2	--	--	3.90	0.10
1.4	--	--	2.10	0.11

Figure 1.

30µm

Backscatter

Composite

Manganese

Magnesium

Figure 2

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 7.