Effect of Oxide Shell Growth on Nano-Aluminum Thermite Propagation Rates

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“There will always be a million reasons not to do something.”

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ABSTRACT

Nanocomposite energetic materials show increased flame propagation rates over their micron scale counterparts. These energetic formulations consist of fuel and oxidizer powder mixtures, commonly referred to as thermites. A theory explaining the faster flame propagation speeds associated with nano-particles is called the melt dispersion mechanism and based on the mechanochemistry of the fuel particle's core-shell structure. The theory supposes that if the ratio (M) of particle radius to shell thickness exceeds a critical threshold, the melt dispersion mechanism is activated, oxidation is accelerated and flame propagation will increase.

This study expands on this theory by growing the oxide shell around aluminum fuel particles in a hot, oxygenated environment to achieve varying M ratios. Flame propagation was examined for untreated and treated aluminum particles in an Al-MoO₃ thermite. Experimental setup consisted of a closed end tube shot and high speed photography. In all cases, alumina shell grew and was damaged due to treatment, and flames rates were reduced. Flame speed of several hundred meters per second, reduction in flame rate with damage to oxide shell, and weak dependence of the flame speed on the ratio M of particle radius to shell thickness in the range $6.1 < M < 13.4$ is consistent with the melt dispersion mechanism of reaction of Al nanoparticles. While the melt dispersion mechanism is activated in an increasing number of particles, the mixture is simultaneously diluted with alumina. This produces an observed plateau, where large changes in shell thickness produce only minor changes in burn rate. Unsteady propagation behavior was observed as the samples were increasingly oxidized. A sharp

drop in flame rate at further reduction in M down to 5 is consistent with a similar drop while adding a similar amount of alumina to the reactive mixture. This indicates that the diluting effect is present.

CHAPTER I

INTRODUCTION

1.1 Background

1.1.1 Aluminum as a fuel

Aluminum has been used as a fuel for over a century [1]. It is a common component of pyrotechnics, fireworks, flares, incendiary devices, propellants and explosives. Among its advantages are that aluminum is inexpensive, available, nontoxic, has a high heat of combustion, and is relatively stable when passivated.

Aluminum will readily react with oxygen to form an oxide as per equation 1.

This oxide is known as aluminum oxide, or alumina, and these terms will be used interchangeably throughout this text. When exposed to the atmosphere, an alumina layer will naturally grow on the aluminum surface. If the aluminum is divided into a powder of spherical particles, then the oxide will form as a shell, as depicted in Fig 1. This shell presents a barrier to further diffusion of oxygen or aluminum and thus limits reaction rates and effectively protects the unreacted aluminum from further oxidation. Powdered and unpassivated aluminum will react with the atmosphere rapidly enough to self ignite

(pyrophoric) so a passivating oxide shell is necessary for aluminum powder to be safely incorporated into a reactive mixture.

Figure 1. Passivation layer of alumina on an aluminum particle.

One category of pyrotechnic mixture is thermites. Thermites are composite energetic materials and are described here as consisting of a metallic fuel (i.e., aluminum, Al) combined with a solid oxidizer (i.e., molybdenum trioxide, MoO₃) [2]. Equation (2) illustrates a typical reaction.

While these formulations have been historically valued for their ability to produce high heats of reaction and combustion temperatures [2], [3], they have been limited in application by their slow reaction rates.

1.1.2 Aluminum nanoparticles

Recent development in processing techniques have allowed for the production of fuel and oxidizer particles into the nanoscale regime. These are particles with features in the range of 1-100 nm. While nanofeatures are described in terms on the nanometer, where $1\text{ nm} = 10^{-9}$ meters, atomic features are described in terms of angstroms, where $1\text{ \AA} = 10^{-10}$ meters.

One method commonly used for the production of nano-particle aluminum is the wire explosion process [4]. This involves discharging a capacitor through an aluminum wire which results in a super heated plasma [5]. As the gaseous aluminum cools and condenses, nanoparticles are formed.

When particles have been shrunk down to the nanoscale, the surface area to volume ratios are greatly increased. Figure 2 shows the surface area to volume ratio as a function of particle diameter as reported by Chaunhan in her master's thesis [6].

Figure 2. Surface area to volume ratio as a function of particle diameter. G. Chauhan, "Influence of Alumina Shell on nano Aluminum Melting Temperature Depression," Texas Tech University, 2007.

This results in the properties of the surface atoms playing a more dominant role in the material properties. These surface atoms have a higher surface energy than the bulk material, which gives them unique properties. Indeed, nano aluminum particles have been shown to exhibit different properties than the bulk material, including decreased activation energies [7–10], as well as decreased melting temperatures [11–13] and melting enthalpy [14]. Additionally, these nanoparticles have been shown to have greatly increased reaction rates, sometimes by an order of magnitude or more [8], [10], [15–18].

1.2 Motivation

These greatly increased reaction rates have provided for essentially a new class of energetic materials. Also known as nano thermites, super thermites, or Metastable Intermolecular Composites (MIC), these new materials have a range of desirable qualities. Nanothermites have the potential to release more than twice the energy of the best molecular explosive [19]. Additionally, they boast smaller quenching diameters, multiple propagation regimes, and an ability to tailor reaction by adjusting stoichiometry, particle size, or by using pretreatment or additives. These reactions can even be valued for their products in biocidal [20] or combustion synthesis applications [21].

Because of these unique properties, nanothermites have the potential to find applications in microthrusters, cutting torches, counter WMD, power systems for MEMs devices, and environmentally friendly initiators for munitions and explosives [22], [23].

Because there is great potential for use of nanothermites in the commercial, industrial and defense sectors, there is a great need to understand the fundamental mechanisms by which these compositions react.

1.3 Aluminum Oxidation Theory

Several researchers have proposed advanced diffusion-based models describing nano-Al particle oxidation. One model proposed by Zachariah and coworkers is based on modification of the diffusion coefficients for metal and oxygen across an oxide shell

nanoparticle through introduction of a convective force driven by a pressure gradient [24], [25].

Another approach taken by Dreizin and coworkers describes oxidation in terms of a series of polymorphic phase transitions within the alumina shell [11], [26–28]. The model emphasizes the thickness dependent multiple phase transitions in alumina during particle heating and predicts complex heating and oxidation kinetics. This model was derived for relatively slow oxidation rates and with experiments involving micron scale particles such that nanoparticle behavior could be extrapolated [11], [29].

1.3.1 The melt dispersion Mechanism

A third model proposed by Levitas et al is based on a mechanochemistry approach and is applicable only at high heating rates [30–33]. The theory describes heating, phase change and rapid pressure buildup within the fuel particle core. The mechanism has been coined the melt dispersion mechanism (abbreviated as MDM) because it results in a burst-like dispersion of molten fuel [19]. More specifically, melting of the Al core is accompanied by a 6% increase in volume which places the oxide shell under tremendous hoop stress. The shell eventually fails and dynamic spallation occurs. After this, unbalance pressure causes an unloading wave propagating to the particle center which generates large tensile pressure and disperses small molten aluminum clusters into the reaction zone. This aluminum would have no protective coating, and thus the reaction would then be kinetically controlled. An illustration of this is shown in Fig 3. In this theory, the key controlling parameter is not the shell thickness or particle size, but

the ratio between the two. This ratio is denoted as M , where R is the Al core radius, δ is the shell thickness, and $M=R/\delta$, as depicted in Fig 4.

Figure 3. Illustration of melt dispersion mechanism

Figure 4. Illustration of M parameter, where $M=R/\delta$.

A significant implication of this theory is that the propagation rate will increase with increasing oxide shell thickness, up to a certain critical value: $M_{\text{crit}} = 19$ [30]. After this point, MDM would be activated and burn rates would be independent of further shell growth. This theory suggests a different approach to processing aluminum powders in which micron particles could potentially perform as well as their nanoscale counterparts as long as they could be synthesized with M values below 19, and entire particles can be made to melt and disperse.

In a recent study [34], an increase in particle reactivity was demonstrated when the alumina shell is pre-compressed and the Al core is pre-expanded. Pre-stressing was produced by heating particles to several elevated temperatures, holding them at a temperature for 10 minutes to relax thermal stresses, and cooling them at several rates to room temperature. For the heating to 105°C and cooling at 0.13°C/s , flame propagation speed increased by 31% for nanoparticles and for 41% for micron particles. These results were quantitatively consistent with the theoretical predictions based on the melt-dispersion mechanism.

As nanoparticles are difficult and expensive to manufacture, the ability to replace them with micron scales particles that perform equally as well would result in enormous savings for the industry.

1.4 Objective

The objective of this study is to examine the propagation rates of an Al + MoO₃ thermite by synthesizing Al particles with controlled and varied oxide shell thicknesses and thus varying M . The synthesis approach is to thermally treat Al particles at temperatures as high as 480°C for up to 180 minutes in a pure oxygen environment and monitor the particle shell thickness using transmission electron microscope (TEM).

Flame propagation rates are measured from high speed video data of powders propagating in a semi-confined tube apparatus; a benchmark diagnostic for comparing thermite formulations [16], [35], [36]. The resultant burn rate trends will be compared to the predictions of both MDM and diffusion theories.

CHAPTER II

EXPERIMENTAL

2.1 Safety

Safety is of paramount importance when in the laboratory and should always be treated as the number one priority. Your safety and the safety of others is your responsibility. A safe and efficient lab requires everyone to do their part. Never be afraid to ask a fellow researcher if you are unsure about a chemical or procedure. In addition to all of the common laboratory hazards, energetic materials present several additional dangers to the researcher. These can be generally divided into two categories: physical dangers and chemical dangers.

2.1.1 Physical Dangers

Nano thermites are unstable mixtures of chemicals and are a sub-category of low order explosives. As such, they will produce explosions when mishandled. Explosions may produce injury through severe burns or throwing fragments. Even small explosions can throw molten metal and other debris. Thermites can be ignited by heat, friction, impact, and static electricity. Always ground yourself before handling reactive mixtures. Even small electric currents can cause accidental ignition. Always wear safety glasses

when handling chemicals or working with tools. Use hearing protection if needed.

Always use a shield to separate yourself from the reaction.

Thermites should only be mixed when wetted with hexanes. If dried on a hot plate, allow the thermite to cool before scraping. Use very gently motions with the brush when sieving. Exercise caution when pressing pellets. The friction created commonly ignites pellets during pressing. Always grind fuel and oxidizers separately.

The researcher should always be prepared for an accidental ignition. Follow all the safety precautions even if you do not anticipate a reaction. Most importantly: **ALWAYS USE SMALL QUANTITIES.** Mix only enough for your test. It is not recommended to exceed 1g. This is the single most effective way to limit the damage from an accidental ignition.

2.1.2 Chemical dangers

The dangers presented by nano thermites are not limited to accidental ignition. Exposure to nanoparticles can have serious health consequences later in life. Nanoparticles are small enough to be absorbed through the skin [37]. They have been shown to accumulate in the vital organs of mammals including the brain, heart, and liver. Nanoparticles are much smaller than the cells in your body, and so are much more difficult to eliminate. Even materials that are inert in bulk form can be hazardous when reduced to the nanoscale [38]. Figure 5 shows a diagram from Buzea et al. that illustrates

the routes of exposure, targeted organs, and related diseases associated with nanoparticles [39].

Figure 5. Diagram of human body with nanoparticle routes of exposure, targeted organs, and related diseases from epidemiological, in vivo and in vitro studies. C. Buzea, I. I. P. Blandino, and K. Robbie, "Nanomaterials and nanoparticles : Sources and toxicity," *Biointerphases*, vol. 2, no. 4, pp. 1-103, 2007.

Limit your exposure by always wearing gloves and avoiding inhalation. Always vent reactions in the fume hood or by using the ventilation ducts. Manipulation can aerate these powders so work should be done in a glove box the fume hood whenever possible. Read the MSDS for any material you plan to use, before you use it. Each chemical presents its own unique dangers, and these must be understood before its use.

Always keep the work area clean and free of clutter. This makes research easier and safer for everyone. Clean any residues to prevent contamination of other people and their belongings. Do not touch anything with dirty gloves, as this will cross contaminate that item.

2.2 Experimental Approach

The experimental approach involved heat treating Al particles in an isothermal furnace to control alumina shell growth. Particles were characterized using a thermogravimetric analyzer (TGA) and transmission electron microscope (TEM). Flame propagation was analyzed using semi-confined flame tubes. Each phase of this study will be described in more detail here.

2.3 Materials

A summary of Al particles prepared in this study is presented in Table 1. Aluminum powder was supplied by Sigma Aldrich with an average particle size of 95 nm and a nominal purity of 99.5%. These particles were treated in a 480°C isothermal environment for up to 180 minutes. The notation Al-0m corresponds to untreated Al as received by the supplier and Al-30m denotes Al particles treated at 480°C for 30 minutes. The reported active content for the Al-0m aluminum was calculated from the measured shell thickness. Molybdenum trioxide (MoO_3) was supplied by Nanostructured & Amorphous Materials, Inc. and combined with Al particles for the flame propagation rate

studies. The MoO_3 particles have an average particle size of 370 nm and are 99.5% active, as reported by the manufacturer.

Table 1. Material properties

Material	Diameter (nm)	Isotherm Time (min)	Shell Thickness (nm)	% Active	M value
Al-0m	95	0	2.7	88.3	16.7
Al-8m	95	8	3.3	86.5	13.4
Al-15m	95	15	4.5	84.4	9.6
Al-30m	95	30	4.6	79.8	9.3
Al-60m	95	60	5.7	75.5	7.3
Al-90m	95	90	6.7	74.1	6.1
Al-150m	95	150	8.3	67.3	5.2
MoO ₃	370	x	x	99.5	x

2.4 Thermogravimetric Analysis

A baseline analysis of Al oxidation was performed using a Netzsch STA 409 PC Luxx thermogravimetric analyzer (TGA). The TGA is capable of measuring mass with a precision of 0.001 mg and thus monitors the weight gain as Al is oxidized to alumina. For this analysis, 11.48 mg of untreated Al was held in a platinum crucible in a controlled environment of ultra high purity oxygen. Pure oxygen was chosen over atmospheric air to prevent any possible reactions with nitrogen or humidity, as aluminum has been shown to form nitrides [40]. The chamber was then heated at a rate of 40°C per minute until the isothermal temperature of 480°C was reached. The isotherm was held for 180 minutes and mass gain monitored.

2.5 Growing the Oxide Shell

The data produced in the TGA analysis provided mass gain and oxidation information to enable larger Al sample sizes to be heat treated in an isothermal furnace by controlling duration of heat treatment. A Neytech Qex oven was used for this purpose. This instrument is shown in Fig 6. A programmable interface allowed for automated control of ramp rate, isotherm time, and purge gas flow, producing consistent and accurate heating profiles. Six samples of Al powder were prepared by oxidation in a pure oxygen environment at 480°C. Different batches were held for lengths of time varying up to 150 minutes. The isotherm temperature of 480°C was chosen because this temperature provided reasonable reactions rates based on several TGA/DSC trial runs that indicated 480°C is high enough to allow oxidation and shell growth to be completed within several hours.

Figure 6. Neytech Qex programmable oven used for Al heat treatment

For each heat treatment, roughly 900 mg of Al powder were prepared. The oven chamber was purged with ultra-high purity oxygen flowing at 180 cc/min for a period of 10 minutes. This allowed for the volume to be flushed 5 times with the purge gas, giving a statistical purity of 99% oxygen in the chamber. The temperature was ramped at a rate of 200 °C/min until the isotherm temperature of 480°C was reached. The temperature was then held constant for different lengths of time, producing Al samples with varying oxide shell thicknesses.

2.6 Transmission Electron Microscopy

A Jeol JEM-2100 high resolution transmission electron microscope (TEM) was used to image the Al particles at 200kv. This thermoionic emission microscope used a LaB6 filament. The particles were dispersed in a methanol solution and then droppered onto a copper disk with a carbon webbing. The grid was allowed to dry before insertion into the TEM. Several particles from each aluminum batch were imaged. Gatan image analysis software was used to measure the oxide shell in three different places for each particle. These values were averaged to give a mean shell thickness. Additionally, roughly 100 particle diameters were measured at lower magnifications giving an average particle diameter of 95nm. This value was close to the statistical median and mode in the size distribution plot.

2.7 Thermite Preparation

Mix weights were calculated to provide a series of thermites with varying alumina portions, but with a constant equivalence ratio of $\Phi = 1.3$. Reactants were first weighed into a plastic cup, then a hexanes solution was added. The mixture was sonicated with a Misonix Sonicator 3000 for 2 minutes, with intervals of 10 seconds on and 10 seconds off. The sonication process uses ultrasonic waves to intimately mix the fuel and the oxidizer. This process has been shown to produce a homogenous mixture, and is widely used in nanothermite preparation [41].

The sonicated solution was poured into a borosilicate glass dish and allowed to evaporate on a hot plate set to about 80°C. The mixture was considered dry ten minutes

after the last visible “wetness” was observed. The dry mixture was sieved through a 355 micron wire mesh to yield a finely powdered thermite.

2.8 Flame Propagation Experiments

Figure 7 is a schematic of the flame propagation rate experiments. A 13 cm long steel tube was drilled through the center with a No. 6 size drill bit. Threads were cut into one end to accept an ignitor and produce closed-end ignition conditions. This tube had a second channel drilled into the side into which an acrylic rod was epoxied. This provided a configuration where the flame front could be viewed through a window while still providing enough mechanical strength to contain the combustion pressures.

Figure 7. Experimental Setup

The thermite was carefully loaded into the steel tube until the powder was flush with the opening. The tube was lightly tapped to reduce density gradients and eliminate air pockets, and then additional powder was loaded into the tube. The tube was weighed before and after powder loading to provide data for charge density. Charge density was fairly consistent around .40 g/cc. The tube was secured to a fixture inside a steel blast chamber with an acrylic window. The ignition system provided current to the filament while simultaneously sending a 0.38 volt signal to the delay generator. The generator then immediately triggered the camera.

A Vision Research Phantom v7.1 high speed camera was used to take high speed video of the combustion event. Video was recorded at 47,000 frames per second at an exposure of 16 μ s. The aperture was usually set at f-stop 8 or 11, depending on the anticipated reaction rate. Higher f-stop settings are recommended to prevent excessive pixel saturation for quicker reactions. The phantom software was used to track the position of the flame front with respect to time. The forward-most saturated pixel was defined as the front of flame propagation. A line was fit through the last four points on each position versus time trace and the slope corresponds with the flame propagation rate.

2.9 Thermal Equilibrium Modeling

The Al-MoO₃ reaction was modeled as a constant volume explosion using thermal equilibrium software, Cheetah [42]. Over a number of iterations, the proportion of alumina in the mixture was incrementally increased while keeping the ratio of aluminum to molybdenum trioxide constant at $\Phi = 1.3$. An initial density of 0.40 g/cc

was chosen as this was a typical density for a loaded tube shot. It was necessary to include a small portion of gas for the code to run. For this purpose .0001% by weight of argon was included in the composition. This analysis enabled a correlation between the combustion properties theoretically predicted and the experimental measurements as a function of alumina content.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Mass Gain

Figure 8 shows Al mass gain over an extended duration at 480°C in a pure oxygen environment.

Figure 8. Aluminum mass gain during Thermogravimetric Analysis and in treated batches

The smooth curve is data taken from the TGA, while the points represent mass gain from the oven heat-treated Al samples. All mass gain is assumed to be from the addition of oxygen.

The transient in the mass gain plot at early times is from a buoyancy effect within the instrument and occurs during the initial temperature ramp. As the purge gas is heated, its density changes which in turn affects the balance readings. Thus, this is an artifact of the process, not a mass fluctuation.

The oven treated Al particles do not align precisely with the TGA data and reflect slightly more mass gain than anticipated from the TGA data. In the TGA, the platinum crucible was covered with a lid containing a pinhole for gas to escape. It is possible that this pinhole was small enough to bottleneck the mass transport of oxygen into the crucible, limiting the oxidation rate. The crucible in the oven was uncovered and therefore would not experience the same constraint. Additionally, while the oven was ramped at a rate of 200°C/min the TGA was ramped at only 40°C/min. This difference in heating rate may also have an effect on oxidation behavior.

Though the mass gain appears to be linear for the time interval used, if the TGA plot were extended, the slope would be seen to decay. This is because the O₂ must diffuse through an ever growing oxide shell barrier which limits the mass transport rates. Eventually the curve would level off as the reaction rate goes to zero. This would indicate the reaction has gone to completion and no unreacted aluminum remains. A final mass gain of 89% would imply an initial active content of 100%.

3.2 Oxide Shell growth

Figure 9 is a TEM micrograph of the Al-60m treated particles. It can be seen that the particles are all roughly spherical in morphology. This is an important prerequisite for the activation of the melt dispersion mechanism.

Figure 9. TEM micrograph of Al-60m particles.

Figure 10 shows the TEM micrographs of an untreated and heat-treated Al particle, respectively. The treated particle was held in a pure oxygen environment at 480°C for 90 minutes. The images show that the oxide shell has grown significantly. The white fringes along the outside of the particle are an optical artifact from interference and are not included in the shell thickness or diameter measurements.

Figure 10. TEM Micrograph of oxide shells on a) Al-0m and b) Al-90m. Scale bars are both 10nm.

Several particles from each batch were imaged, and for each particle the shell was measured 3 times. Measurements were taken only of particles that were not overlapping. These values were then averaged together. Lower magnification images were taken of clusters of particles. The diameters of roughly 100 of these particles were then measured and these values were averaged together. This produced an average diameter of 95 nm for the aluminum powder. The particle size distribution histogram is shown in Fig 11. It can be seen that the mean average particle size corresponds closely to the median.

The standard deviation from the 95nm average was 45 nm. While this could conceivably introduce a large error in the M calculations, one must keep in mind that MDM is based on averages. So although the value of 95nm represents a large range of particle sizes, the average value of 95nm is consistent and accurate from batch to batch.

Figure 11. Histogram of particle size distribution. Diameter values were measured in TEM.

The thickness of the oxide layer can be estimated using equation (3) given the percent aluminum content and densities of the metal and metal oxide.

$$\frac{R^3}{(R - \delta)^3} = \frac{\rho_m}{\rho_{mo}} \left(\frac{1}{1/Y - 1} \right) + 1 \quad (3)$$

In Eq. (1) R is the radius of the spherical particle, δ is the thickness of the oxide layer, ρ is the density of the metal (m) or metal oxide (mo), and Y is the mass fraction of metal oxide to total particle mass, as derived from the active content. The oxide shell was measured on the untreated aluminum to be 2.7 nm. Using the equation above, and

assuming a diameter of 95nm, it can be calculated that the untreated powder was an average of 88.3% pure aluminum. This initial aluminum content was then used to estimate the shell thicknesses for a given mass gain. These estimates along with the measured shell thickness are reported in Fig 12.

Figure 12. Measured Oxide shell thickness for treated aluminum with predicted shell thickness as expected from mass gain. Triangles indicate measured thicknesses, while circles indicate calculated thicknesses.

It can be seen that the oxidation rate decreases with time. As the oxide shell grows, it presents a barrier to the diffusion of aluminum cations, thus limiting the oxidation rate and growth rate of the shell. Though the mass gain data is roughly linear, the oxide shell thickness are not. This is expected as the mass gain is a function of shell mass while the thickness is a function of shell volume.

While the Al-15m batch has a weight gain in line with the other data (see Fig. 8), the shell thickness is unexpectedly large, as seen in Fig 12. Re-imaging this batch of particles in the TEM confirmed the original shell thickness measurement. This can be explained as follows. The cooling down to the room temperature generates large internal stresses, which lead to cracking of the shell and possible delamination of the shell from the core. In case of delamination, it may even lead to ignition during the cooling, as it was reported for micron particles in [43]. In our case, while ignition was not observed, significant weight gain after heat treatment suggests significant distributed cracking of the oxide shell.

Similar consideration about increase in stress-free temperature T_0 is valid for particles oxidized in an oven or TGA. However, due to volume increase during chemical reaction, additional stresses appear, which may not relax during holding at 480°C. On the other hand, after cooling total stresses and extend of damage in oxidized particles may be smaller than in not oxidized, because oxidized particles have larger shell thickness.

A second phenomenon may also be involved in the cracking of the oxide shell. It has been reported [26], [44] that the oxide shell undergoes a phase transition from an amorphous to a crystalline structure during the growth process. This process is illustrated by the schematic in Fig 13.

Figure 13. Oxide shell growth on aluminum particle.

In the temperature range used, the $\gamma\text{-Al}_2\text{O}_3$ phase of alumina is thermodynamically favorable [45]. However, due to surface interactions with the aluminum, the Al_2O_3 exists in the amorphous phase until a critical thickness of roughly 4 nm is reached. At this point the oxide transitions to the $\gamma\text{-Al}_2\text{O}_3$ phase which has a lower specific volume than the amorphous phase [26].

This may or may not potentially lead to a cracked shell, depending on whether change in volume occurs isotropically or just reduces the shell thickness without causing significant hoop stresses [31]. If the phase change is isotropic, the new growth only partly covers the aluminum core, leading to a cracked shell. These cracks provide a channel of least resistance for the diffusion of aluminum and oxygen ions, allowing these areas to oxidize more quickly than those covered with a thick shell. In this way, the cracks fill in with alumina and undergo a “healing” process.

The Al-15m particles were the first batch to transition past this critical thickness of 4 nm. The batches treated beyond this point would have had time for the shell to heal in the oven, which, presumably, would be relatively quick in the hot, oxygenated

environment. The Al-15m batch, however, was taken out of the oven shortly after the phase transition. It is possible that when this batch was weighed, the shell was still in the healing process, and continued to react with the ambient environment after being weighed. Also, shell after 15 minute was relatively thin, and total stresses therefore are higher than for larger shell, leading to more intense damage. This would explain why the shell growth is beyond what would be expected from the measured mass gain.

Thus, a damage to oxide shell is expected for all particles: (a) due to thermal stresses at cooling down from 480°C to room temperature; (b) due to change in volume during reaction, and (c) due to phase transformation in a shell.

3.3 Flame Propagation Rates

3.3.1 Comparison with Cheetah

The flame propagation rates for the treated Al are shown in Fig. 14 along with the pressure calculations from Cheetah. The high speed videos were each analyzed three times and the resultant burn rates averaged together. The human error in the flame speed diagnostic was found to have a standard deviation of 6 m/s. These error bars are small enough to be covered up by the icons themselves.

The pressure estimates from Cheetah can be seen to drop off quickly as the mixture is diluted with alumina. This is likely due to a combination of decreased gas production and lower temperatures.

Figure 14. Burn rates of as a function of active aluminum content with constant volume pressure as predicted by Cheetah. Equivalence ratio of $\Phi = 1.3$.

It can be seen that flame propagation rates also decrease as active Al content is reduced (i.e., greater presence of alumina). Overall, the decreasing trend is consistent with diffusion theory, as thicker shells will hinder oxygen diffusion to the core of the Al particle. Also, the alumina that is added to the system is inert and acts as a heat sink, decreasing reaction temperatures and slowing the reaction kinetics.

Furthermore, each unit volume (or mass) of thermite will contain less moles of reactants. This will in turn produce less gas, and lower pressures, as reported by Cheetah. Aluminum based nanoparticle thermites, including $\text{Al}+\text{MoO}_3$, have been conjectured to propagate by convective energy transfer [16], [35]. With less gas produced at a lower pressure, convection may be hindered resulting in slower propagation rates. It should be noted that Cheetah is a thermochemical equilibrium code and would not reflect the more intimate physics the Melt Dispersion Mechanism.

3.3.2 Comparison with melt dispersion mechanism

To compare the burn rates results with the predictions of MDM, the burn rates were plotted as a function of M in Fig 15. Recall M is defined as:

$$M = R/\delta \quad (4)$$

where, R is Al core radius and δ is alumina shell thickness.

Figure 15. Burn rates as a function of M value. The point at $M=17$ is the untreated aluminum.

The maximum propagation rate is for untreated particles, 682 m/s is close to the 627 ± 19 m/s that has been previously reported for this mixture [34]. For any M , flame propagation speeds are well above 10 m/s, which is too high for diffusion mechanism but provides required heating rates for activation of melt dispersion mechanism [46]. Any treatment of particles leading to $6.1 < M < 13.4$ reduced flame rate down to $315 < V < 392 \pm 6$

m/s, which is consistent with the suppression effect of damage to oxide shell on the melt-dispersion mechanism [46]. Doubling the shell thickness from 3.3nm (Al-8m) to 6.7nm (Al-90m) only depressed the flame rate about 20% (from 392 m/s to 317 m/s, respectively), producing the predicted plateau. The fact that the flame rate is almost constant in the range $6.1 < M < 13.4$ also consistent with predictions based on melt dispersion [32][32].

Note that the actual prediction based on melt dispersion mechanism is that with decreasing M , flame rate reaches its maximum when the entire melt is dispersed and participates in reaction, and cannot grow further because there is nothing to improve anymore. At the same time, reduction in flame rate after reaching maximum does not contradict the melt dispersion mechanism. By decreasing M , active aluminum content, gas generation, and consequently pressure are reduced (as reported by Cheetah, Fig. 14), which may suppress convective mechanism of flame propagation. Also, the alumina that is added to the system is inert and acts as a heat sink, decreasing reaction temperatures and slowing the reaction kinetics. The fact that in all previous experiments with undamaged particles [30], [32], flame rate does not change for $10 < M < 19$ and is at the level of 950 m/s means that the effect of reaction mechanism was much stronger than the propagation mechanism and reduced Al content and gas pressure. For the damaged particles here, there is some small reduction in the flame rate in the range $6.1 < M < 13.4$.

The melt dispersion mechanism theory predicts that propagation rate (V) for M values greater than the critical value of $M_{crit} = 19$ will steadily increase as M approaches

19. For $M < 19$, the maximum V is achieved and plateaus such that further decreases in M do not correspond to increases in V [30].

The trends observed seem to be best explained with a combination of both theories. Because of the particle size distribution, as the shell is grown, more and more particles are brought past the M_{crit} value where MDM would be activated. The smaller particles that are already below M_{crit} would not be affected by the growing shells (recall the plateau below $M = 19$) while the larger particles would approach M_{crit} . Thus, overall, MDM would be activated in a larger fraction of total Al particles with increased treatment. This should work to increase reaction rates. At the same time, more Al_2O_3 is being added to the system and its dilutant heat sink effects will act to suppress burn rates. Also the number of reactive moles per unit volume or weight are also being reduced, thus gas production is being reduced. These competing phenomena appear to more or less cancel each other out over a certain range of M .

3.3.3 Observed Shell Cracking

The shells were observed to burst in some particles after treatment. Figure 16 shows a micrograph of untreated particles (Al-0m) on the left, with treated particles (Al-150m) that contain an example of the burst shell. This cracking behavior has been observed previously, when particles were progressively heated past their melting point in a hot stage TEM [28], [44]. In reviewing the TEM micrographs, it was observed that while the burst particles were only a small fraction of the whole, their occurrence was more prominent in the longer treated aluminum batches.

Figure 16. Observed oxide shell cracking. Left: Al-0m Right: Al-150m

3.3.4 Ignition Difficulty in Highly Oxidized Aluminum

It is noted that the Al-150m thermite did not readily ignite with the steel filament used for the other tests. More than one attempt was necessary to initiate the tube shot. When a pea-sized amount of the other mixtures were exposed to an open flame they would readily ignite with a pop. However the Al-150m thermite was observed to react only after being exposed to an open flame for several seconds. It is interesting to note that the thermite with the slowest propagation rate was also the most difficult to ignite.

For Al-150m Al content is around 67%, and a sharp drop in flame rate occurs down to 53 ± 6 m/s. Note that similar drop was observed for undamaged particles in [47], [48] when added percentage of alumina to reactive mixture was between 15% and 20%. These numbers are close to the increase in alumina percentage due to shell growth in this experiment.

3.4 Unsteady Propagation

Unsteady propagation has been observed when aluminum based nano-thermites are mixed to sub-optimal equivalence ratios or diluted with alumina. Instead of a steadily accelerating flame front, these unsteady propagations are characterized by swirling, oscillating and jumping motions of the reaction front [27], [28]. Thermites mixed at sub-optimal equivalence can be thought of as diluted by either excess fuel or oxidizer. In a similar way, as the thermites were diluted with the addition of alumina in the shell, they exhibited the same unsteady propagation patterns. The heat-treated Al thermites demonstrate this unsteady propagation behavior. Figure 17 shows the position versus time plots for the untreated and heat treated Al thermites, respectively. Part a) is of the untreated Al/MoO₃ thermite, while part b) is from a thermite mixture using aluminum heated in pure oxygen for 1.5 hours.

Figure 17. X-t traces of flame front. Right: Untreated aluminum. Left: Al-90m

The breaks in the second trace exemplify the jumping behavior. In the video, the flame front can be seen to propagate forward for a distance and then appears to be stationary. Luminosity then re-emerges at a further point along the tube. That the treated mixtures would exhibit the same behavior as diluted mixtures indicates that the oxide shells do have a diluting effect in the reaction.

CHAPTER IV

CONCLUSIONS

The melt dispersion mechanism is one theory proposed to describe the oxidation of nanometric aluminum. In this theory the aluminum core melts, increasing pressure inside the particles. The oxide shell contains this pressure until the mechanical stress limits of the shell are exceeded. At this point, the particle dynamically spallates, dispersing molten, unpassivated aluminum into the reaction zone.

This theory was investigated by synthesizing nano aluminum particles with different oxide shell thicknesses, producing batches of aluminum with a range of M values. The chosen heat treatment at 480°C damages alumina shell due to several possible reasons: (a) due to thermal stresses at cooling down from 480°C to room temperature; (b) due to change in volume during reaction, and (c) due to phase transformation in a shell. This damage reduces flame speed.

When incorporated into an Al-MoO₃ thermite composition, the burn rate trends are best explained by the predictions of diffusion theory and the melt dispersion mechanism theory. The competing effects of each mechanism appear to produce a range of M values where thermite propagation rate is only mildly affected by a significant increase in shell thickness

Flame speed of several hundred meters per second, reduction in flame rate with damage to oxide shell, and weak dependence of the flame speed on M in the range $6.1 < M < 13.4$ is consistent with the melt dispersion mechanism of reaction of Al

nanoparticles. When percentage of alumina exceeds a threshold of about $30\% \pm 3\%$, flame rate sharply drops, which is consistent with results from Foley et al. [48]. This gave rise to unsteady, jumping flame fronts, as previously observed when bulk alumina was added to the system. This is evidence that increasing the oxide shell produces a diluting effect.

In future experiments, to avoid or reduce damage to oxide shell, temperature for treatment will be reduced. Alternatively, while keeping this temperature for oxidation to provide relatively fast kinetics, cooling down will be performed much slower, to relax stresses. It can be done down to the chosen temperature T_0 (temperature at which particle is stress-free), followed by fast cooling down to room temperature, in order to create pre-stressing similar to that done previously [34].

Future work could include XRD of aluminum batches to confirm crystal structure and to measure evolution of internal stresses. Also, measuring weight continuously over the course of hours/days/ will allow for the quantitative analysis of reaction progress of the the damaged particles. Starting with larger (micron) scale particles would expand the M value range that can be investigated.

BIBLIOGRAPHY

- [1] X. Y. Yuan, C. B. Zhan, H. B. Jin, and K. X. Chen, "Novel method of thermite welding," *Science And Technology of Welding and joining*, vol. 15, no. 1, pp. 54-59, 2010.
- [2] L. L. Wang, Z. a. Munir, and Y. . Maximov, "Review Thermite reactions: their utilization in the synthesis and processing of materials," *Journal of Materials Science*, vol. 28, pp. 3693-3708, 1993.
- [3] S. . Fischer and G. M.C, "Theoretical Energy Release of Thermites, Intermetallics and Combustible Metals," in *24th International Pyrotechnics Seminar Conf -9807*, 1998.
- [4] R. Sarathi, T. K. Sindhu, and S. R. Chakravarthy, "Generation of nano aluminium powder through wire explosion process and its characterization," *Materials Characterization*, vol. 58, pp. 148-155, 2007.
- [5] B. R. Turner, "A study of exploding bridgewires," PhD diss., California Institute of Technology, 1960.
- [6] G. Chauhan, "Influence of Alumina Shell on nano Aluminum Melting Temperature Depression," Thesis, Texas Tech University, 2007.
- [7] C. E. Aumann, G. L. Skofronick, and J. A. Martin, "Oxidation behavior of aluminum nanopowders," *Journal of Vacuum Science and Technology B*, vol. 13, no. 3, pp. 1178-1183, 1995.
- [8] K. Park, D. Lee, A. Rai, D. Mukherjee, and M. R. Zachariah, "Size-Resolved Kinetic Measurements of Aluminum Nanoparticle Oxidation with Single Particle Mass Spectrometry," *Journal of Physical Chemistry*, vol. 109, pp. 7290-7299, 2005.
- [9] E. M. Hunt and M. L. Pantoya, "Ignition dynamics and activation energies of metallic thermites: From nano- to micron-scale particulate composites," *Journal of Applied Physics*, vol. 98, no. 3, p. 034909, 2005.
- [10] A. Pivkina, Y. Frolov, and D. Ivanov, "Nanosized components of energetic systems: Structure, thermal behavior, and combustion," *Combustion, Explosion, and Shock Waves*, vol. 43, no. 1, pp. 51-55, 2007.

- [11] M. A. Trunov, S. M. Umbrajkar, M. Schoenitz, J. T. Mang, and E. L. Dreizin, "Oxidation and melting of aluminum nanopowders.," *The journal of physical chemistry. B*, vol. 110, no. 26, pp. 13094-9, Jul. 2006.
- [12] J. Sun and S. L. Simon, "The melting behavior of aluminum nanoparticles," *Thermochimica Acta*, vol. 463, pp. 32-40, Oct. 2007.
- [13] J. Eckert, J. Holzer, C. Ahn, and Z. Fu, "Melting behavior of nanocrystalline aluminum powders," *Nanostructured materials*, vol. 2, pp. 407-413, 1992.
- [14] Z. Zhang, X. X. Lu, and Q. Jiang, "Finite size effect on melting enthalpy and melting entropy of nanocrystals," *Physica B*, vol. 270, pp. 249-254, 1999.
- [15] J. Sun, M. L. Pantoya, and S. L. Simon, "Dependence of size and size distribution on reactivity of aluminum nanoparticles in reactions with oxygen and MoO₃," *Thermochimica Acta*, vol. 444, pp. 117-127, 2006.
- [16] M. R. Weismiller, J. Y. Malchi, J. G. Lee, R. A. Yetter, and T. J. Foley, "Effects of fuel and oxidizer particle dimensions on the propagation of aluminum containing thermites," *Proceedings of the Combustion Institute*, vol. 33, no. 2, pp. 1989-1996, 2011.
- [17] J. A. Puszynski, "Processing and characterization of aluminum-based nanothermites," *Journal of Thermal Analysis and Calorimetry*, vol. 96, no. 3, pp. 677-685, Jul. 2009.
- [18] Q. Kwok, R. C. Fouchard, A. Turcotte, P. D. Lightfoot, R. Bowes, and D. Jones, "Characterization of Aluminum Nanopowder Compositions," *Propellants, Explosives, Pyrotechnics*, vol. 27, pp. 229-240, 2002.
- [19] D. D. Dlott, "Thinking big (and small) about energetic materials," *Materials Science and Technology*, vol. 22, no. 4, pp. 463-473, 2006.
- [20] B. R. Clark and M. L. Pantoya, "The aluminium and iodine pentoxide reaction for the destruction of spore forming bacteria," *Physical Chemistry Chemical Physics*, vol. 12, pp. 12653-12657, 2010.
- [21] A. Varma, "Form from Fire," *Scientific American*, vol. 283, no. 2, pp. 58-61, 2000.
- [22] K. S. Martirosyan, L. Wang, A. Vicent, and D. Luss, "Nanoenergetic Gas-Generators : Design and Performance," *Most*, vol. 34, pp. 532-538, 2008.
- [23] A. W. Miziolek, "Nanoenergetics: An emerging technology area of national importance," *The AMPTIAC Newsletter*, vol. 6, no. 1, 2002.

- [24] S. Chowdhury, K. Sullivan, N. Piekiet, L. Zhou, and M. R. Zachariah, "Diffusive vs Explosive Reaction at the Nanoscale," *The Journal of Physical Chemistry C*, vol. 114, no. 20, pp. 9191-9195, May 2010.
- [25] A. Rai, K. Park, L. Zhou, and M. R. Zachariah, "Understanding the mechanism of aluminium nanoparticle oxidation," *Combustion Theory and Modelling*, vol. 10, no. 5, pp. 843-859, 2006.
- [26] M. Trunov, M. Schoenitz, X. Zhu, and E. Dreizin, "Effect of polymorphic phase transformations in AlO film on oxidation kinetics of aluminum powders," *Combustion and Flame*, vol. 140, no. 4, pp. 310-318, Mar. 2005.
- [27] M. A. Trunov, M. Schoenitz, and E. L. Dreizin, "Effect of polymorphic phase transformations in alumina layer on ignition of aluminium particles," *Combustion Theory and Modelling*, vol. 10, no. 4, pp. 603-623, Aug. 2006.
- [28] A. Rai, D. Lee, K. Park, and M. R. Zachariah, "Importance of Phase Change of Aluminum in Oxidation of Aluminum Nanoparticles," *Journal of Physical Chemistry*, vol. 108, no. 39, pp. 14793-14795, 2004.
- [29] M. Schoenitz, B. Patel, O. Agboh, and E. L. Dreizin, "Oxidation of aluminum powders at high heating rates," *Thermochimica Acta*, vol. 507-508, pp. 115-122, Aug. 2010.
- [30] V. I. Levitas, M. L. Pantoya, and B. Dikici, "Melt dispersion versus diffusive oxidation mechanism for aluminum nanoparticles: Critical experiments and controlling parameters," *Applied Physics Letters*, vol. 92, no. 1, p. 011921, 2008.
- [31] K. W. Watson, M. L. Pantoya, and V. I. Levitas, "Fast reactions with nano- and micrometer aluminum: A study on oxidation versus fluorination," *Combustion and Flame*, vol. 155, no. 4, pp. 619-634, Dec. 2008.
- [32] V. I. Levitas, B. W. Asay, S. F. Son, and M. Pantoya, "Mechanochemical mechanism for fast reaction of metastable intermolecular composites based on dispersion of liquid metal," *Journal of Applied Physics*, vol. 101, no. 8, p. 083524, 2007.
- [33] V. I. Levitas, B. W. Asay, S. F. Son, and M. Pantoya, "Melt dispersion mechanism for fast reaction of nanothermites," *Applied Physics Letters*, vol. 89, no. 71909, pp. 1-4, 2006.
- [34] V. I. Levitas, B. Dikici, and M. L. Pantoya, "Toward design of the pre-stressed nano- and microscale aluminum particles covered by oxide shell," *Combustion and Flame*, vol. 158, no. 7, pp. 1413-1417, Jul. 2011.

- [35] 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*, vol. 32, no. 2, pp. 1895-1903, 2009.
- [36] B. Dikici, M. L. Pantoya, and V. Levitas, "The effect of pre-heating on flame propagation in nanocomposite thermites," *Combustion and Flame*, vol. 157, no. 8, pp. 1581-1585, Aug. 2010.
- [37] M. Crosera, Æ. M. Bovenzi, and Æ. G. Maina, "Nanoparticle dermal absorption and toxicity : a review of the literature," *Health (San Francisco)*, pp. 1043-1055, 2009.
- [38] A. M. Schrand, M. F. Rahman, S. M. Hussain, J. J. Schlager, D. A. Smith, and A. F. Syed, "Metal-based nanoparticles and their toxicity assesment," *John Wiley & Sons, Inc*, vol. 2, pp. 544-568, 2010.
- [39] C. Buzea, I. I. P. Blandino, and K. Robbie, "Nanomaterials and nanoparticles : Sources and toxicity," *Biointerphases*, vol. 2, no. 4, pp. 1-103, 2007.
- [40] A. Gromov and V. Vereshchagin, "Study of aluminum nitride formation by superfine aluminum powder combustion in air," *Journal of the European Ceramic Society*, vol. 24, pp. 2879-2884, Aug. 2004.
- [41] E. L. Dreizin, "Metal-based reactive nanomaterials," *Progress in Energy and Combustion Science*, vol. 35, no. 2, pp. 141-167, Apr. 2009.
- [42] K. Glaesemann and L. E. Fried, "Recent Advances in Modeling Hugoniot with Cheetah," in *Shock Compression of Condensed Matter*, 2006, pp. 1503-1506.
- [43] V. Rosenband, "Thermo-mechanical aspects of the heterogeneous ignition of metals," *Combustion and Flame*, vol. 137, pp. 366-375, 2004.
- [44] D. A. Firmansyah et al., "Microstructural Behavior of the Alumina Shell and Aluminum Core Before and After Melting of Aluminum Nanoparticles," *Journal of Physical Chemistry*, vol. 116, pp. 404-411, 2012.
- [45] J. M. Andersson, "Controlling the Formation and Stability of Alumina Phases," Linkoping University, 2005.
- [46] 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.

- [47] J. Malchi, R. Yetter, T. Foley, and S. Son, "The Effect of Added Al_2O_3 on the Propagation Behavior of an Al/CuO Nanoscale Thermite," *Combustion, Science and Technology*, vol. 180, pp. 1278-1294, 2008.
- [48] T. J. Foley, A. N. Pacheco, V. E. Sanders, S. F. Son, and B. W. Asay, "The effect of added alumina on the propagation behavior of the nanoaluminum and molybdenum (VI) oxide system," *13th Int. Det. Symp.*, pp. 1217-1228, 2006.
- [49] 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 / MoO_3 , Al / WO_3 , Al / CuO, and Bi_2O_3)," *Journal of Propulsion and Power*, vol. 23, no. 4, pp. 707-714, Jul. 2007.