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Combustion Behaviors Resulting from Bimodal Aluminum Size Distributions in Thermites

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Studies that replace a portion of the micron-size aluminum (Al) with nano-Al particles in an energetic formulation demonstrate significant performance enhancement. Little is known, however, about the critical level of nano-sized fuel particles needed to enhance the performance of the energetic composite. Ignition sensitivity and combustion velocity experiments were performed using a thermite composed of Al and molybdenum trioxide (MoO_3). Both loose powders and compressed pellets were examined. A bimodal Al particle size distribution was prepared using 4 or 20-μm-diam Al fuel particles that were replaced in 10% increments by 80-nm-diam Al particles until the fuel was 100% nano-Al. Results show that with only 20% nano-Al content, the mixtures showed reduced ignition delay times by up to 2 orders of magnitude. The combustion velocity was shown to dramatically increase as more nano-Al particles replace micron-Al particles within the mixture. This increasing trend was attributed to incomplete reactions of the micron-Al particles or significantly slower reactions such that the micron-Al particles promote cooling or quenching of the reaction.

I. Introduction

IN a study by Popenko et al. [1], a mixture of nano-Al powder was combined with micron-Al powder for an examination of the effect of a bimodal Al distribution on the combustion behavior in air. They analyzed the presence of bound nitrogen in the products of bimodal Al and air combustion and found that for mixtures consisting of less than 70% micron-Al powder the percent of bound nitrogen remained constant [1]. The interesting finding was that the bound nitrogen content in the combustion products of these mixtures decreased considerably if the nano-Al concentration in the mixture was less than 20% and this behavior was attributed to the concurrent processes of sintering and incomplete combustion [1].

Using nano-Al combined with micron-Al particles in rocket propellant applications offers advantages. For example, Al particles are passivated with an unreactive oxide shell (e.g., Al_2O_3). As the particle surface area to volume ratio increases the presence of Al_2O_3 increases and becomes a significant portion of the overall mixture. Because propellant payloads can be restrictive, the unwanted levels of an unreactive oxide that may add weight and reduce energy density are undesirable [2]. For this reason, adding small amounts of nano-Al to micron-Al particles may facilitate increased reactivity without the unwanted burdens of excessive amounts of Al_2O_3. In a study by Dokhan et al. [3] the burning behavior of ammonium perchlorate (AP) solid propellant with bimodal Al particle size distributions was examined. They showed a significant increase in burn rate with only a 20% addition of nano-Al (80% micron-Al). At this level, Dokhan et al. [3] showed Al combustion takes place closer to the propellant burning surface allowing increased radiative and conductive heat feed back that increases the temperature at the burning surface, which increases the burn rate.

Thermites, like propellants, are a heterogeneous mixture of fuel and oxidizer particles. A recent surge of interest is focused on developing thermites that may replace traditional lead-based compounds in gun primers [4]. Granier and Pantoya [5] examined the ignition and combustion velocity of $Al + MoO_3$ thermites as a function of Al particle size. Their work showed that reducing the Al particle size to nano dimensions decreased the ignition delay time by 3 orders of magnitude (from 10 s to 10 ms). The combustion velocity of this thermite also exhibits unique behaviors and are a strong function of the bulk density. When bulk density increases, the combustion velocity of a nanocomposite will decrease whereas a micron-composite will increase [6]. This study examines the ignition sensitivity and combustion velocity of $Al + MoO_3$ as a function of the Al particle size distribution. Mixtures are prepared using 4 or 20 μm Al combined with 80 nm Al particles in discrete mixture ratios. The goal is to investigate the influence of nano-Al on the ignition sensitivity and combustion velocity of thermites.

II. Experimental

A. Sample Preparation

Table 1 shows physical data for the Al particles and the supplier for the Al and MoO_3. The Al particles are encapsulated within a protective Al_2O_3 shell. The active Al content is the percent of Al powder that is not in the form of Al_2O_3. As can be seen with the 80-nm-diam Al powder, the Al_2O_3 shell becomes an appreciable portion of the total powder, causing the active Al content to reduce to only 73% (Table 1). The average particle size is calculated from surface area measurements using a gas adsorption analyzer and Brauner Emmitt Teller (BET) theory.

Aluminum was mixed with MoO_3 in a 40/60 weight % ratio which corresponds to a fuel rich equivalence ratio of 1.3, based on active Al content. This mixture ratio was shown to be an optimal composition for achieving the highest combustion velocity and shortest ignition delay time [5]. This equivalence ratio accounts for changing active aluminum content associated with the percentage of nano-Al powder used in each sample. The powders were dispersed in hexanes and sonicated to break up agglomerates and ensure a homogeneous mixture. The mixture was poured into a tray and slightly heated to allow hexanes evaporation.

For pellet tests, a well-mixed, dried powder was separated into 230–270 mg quantities and cold pressed with a hydraulic press and a

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Table 1 Reactant particle descriptions

Particle diameter and description	% Active Al content	Supplier
80 nm Al	73	Nanotechnolgies, Inc. (Austin, TX)
4 μm Al	91	Alfa Aesar (Ward Hill, MA)
20 μm Al	99	Sigma Aldrich (St. Louis, MO)
MoO_3	N/A	Technanogy, Inc. (Santa Clara, CA)

uniaxial die. All final pellets were 6.5 mm in diameter and 3.9 mm in length. Theoretical maximum density (TMD) calculations are based on the weighted average of Al, MoO_3, and Al_2O_3 present in the mixture. For pellets, the powders were pressed to a TMD of 50% (≈ 2 g/cm^3) whereas powders were packed to 5% TMD (≈ 0.2 g/cm^3).

Eleven mixtures of $Al + MoO_3$ were prepared, each with a varying distribution of Al particle size ranging from 100% nano to 100% micron in 10% increments.

B. Ignition and Combustion Velocity of Pellets

The pellets were ignited using a 50-W CO_2 laser (Universal Laser Systems, Inc, Scottsdale, Arizona). A power meter and associated optics were used to monitor the laser power and align the laser beam with the front face of the pellet, respectively. Ignition and flame propagation were recorded using a Phantom IV (Vision Research, Wayne, New Jersey) high-speed camera which captures images at 32,000 frames per second (fps). Details of this experimental apparatus are discussed elsewhere [5].

Ignition is defined as the first appearance of light and onset of a fully sustained self-propagating reaction. This definition is distinctly different than initiation which can be defined as the onset of the first reaction or set of reactions. Dlott [7] showed that for nano-Al particles imbedded in a nitrocellulose matrix the first detection of nitro consumption occurred at roughly 300 ps whereas ignition by first light was not detected until 2 ns. In the present study only ignition was analyzed and detailed analysis of initiation reactions were not resolved. There are several techniques for measuring an ignition delay time [5]. The technique applied here is based on the "first-light" approach in which ignition time is determined as the time lapse between sample exposure to the laser beam and detection of the first light. This may not guarantee ignition (self-sustained combustion) but is a commonly used technique for experimentally determining ignition times. The high-speed camera is synchronized with the CO_2 laser and detects light intensity. In this way, the reaction light is used as the illuminating source to visualize the ignition process.

In thermite combustion, the flame appears to travel in a uniform plane axially consuming reactant particles packed in a highly porous matrix. Flame spreading down the sides was not observed but has been observed with other energetic materials such as explosives [8]. Because the physics of flame propagation in this arrangement entails flame spreading uniformly through the matrix and is a strong function of the packing arrangement of particles and porous structure of the material, the term combustion velocity is used to characterize the speed of the leading edge of the reaction zone identified by visible light emission recorded from the high-speed photographic data. The combustion velocity in these experiments has been shown to be a steady-state measurement. The Phantom imaging software uses a pixel light intensity threshold and the elapsed time between frames to calculate the combustion velocity.

C. Ignition of Loose Powders

A Coherent 250-W CO_2 laser (Santa Clara, California) was used to ignite the powder samples. A NaCl beam splitter (Vigo Photovoltaic, Warsaw, Poland) diverted 8% of the laser beam to a trimetal detector used to determine the time of the start of the laser pulse. A Thorlabs DET210 photo-diode (Newton, New Jersey) with a response time of 1 ns measured light intensity of the reaction and determined the ignition time, based on a Tektronix (Richardson, Texas) oscilloscope with a response time of 1 ns.

D. Combustion Velocities of Loose Powders

A piezo-electric starter ignited a powder mixture (120 mg) poured into the tray and unconfined. A profiling glide leveled a consistent cross section throughout the sample. The pour density of the powder was about 0.02 g/cm^3 corresponding to a TMD of 5%. As the reaction progressed inside the tray, two holes, 0.1 cm in diameter, in the bottom of the tray, which were 2 cm apart, transmitted light from the reaction into fiber optic cables. Photo-diodes were used to convert this light pulse to a voltage that was displayed on an oscilloscope. The average velocity was determined from the two voltage pulses on the oscilloscope. The time of reaction propagation between the holes was determined by the time delay between the two voltage pulses. Because of the small size of the hole, the voltage pulses did not occur until the reaction passed directly over the pinholes. The average velocity was calculated by dividing the distance between the holes by the time of reaction propagation between the holes.

E. Pressure Cell Tests

For the pressure cell experiments, a YAG Continuum MiniLite 100 mJ laser (Santa Clara, California), by way of a Thorlabs fiber optic cable, was used to ignite the samples inside a parr-bomb type chamber. An aluminum cup contained the mixture at a constant volume of 0.151 cm^3. A PCB Piezotronics (Depew, New York) pressure transducer, with a response time of 1 μs, was used to determine maximum pressure output for each test. More details on this apparatus and a schematic diagram are presented in [9].

III. Results

A. Ignition Delay Time

Figures 1a–1c show ignition delay time as a function of percent 80 nano-Al content mixed with MoO_3. Figure 1a combines the nano-Al with 4 μm Al at 50 W laser power, whereas Fig. 1b shows nano-Al combined with 20 μm Al at 50 W laser power and both figures are for pellets. Figure 1c is ignition delay for loose powders of 4 or 20 μm Al at 50 or 100 W laser power. The standard deviation bars represent the range of measurements for 4–6 pellets from each of the 11 bimodal mixtures; the data symbol corresponds to the average ignition delay time. These ignition times for all mixtures containing nano-Al are consistent with previous ignition time measurements made by Granier and Pantoya [5]. The ignition delay time was found to be independent of nano-Al content for mixtures containing at least 20% nano-Al.

Figure 1 quantifies that adding nano-Al particles to a micron-Al mixture reduces the ignition delay time by a factor of 100 for the 4 μm bimodal mixture and a factor of 1000 for the 20 μm Al bimodal mixture. This is likely attributed to the lower ignition temperature required by the nano-Al particles independent of micron-Al presence. For example, based on inert heating up until ignition, the ignition temperature can be estimated from a semi-infinite solid analysis. An analytical solution is derived for a semi-infinite solid exposed to a constant surface heat flux (CO_2 laser irradiation). Equation (1) is the 1-D heat diffusion equation [10]. Boundary conditions are applied for a constant uniform heat flux [Eq. (2)] and assuming an initial temperature (T_i) [Eq. (3)].

$$\frac{\partial T}{dt} = \alpha \frac{\partial^2 T}{dx^2} \tag{1}$$

$$-k \frac{\partial T}{\partial x}\bigg|_{x=0} = q''_o \tag{2}$$

$$T(x,0) = T_i \tag{3}$$

The energy input is greatest at the front surface and ignition is most likely to occur there first (i.e., at $x = 0$). With this simplification, the

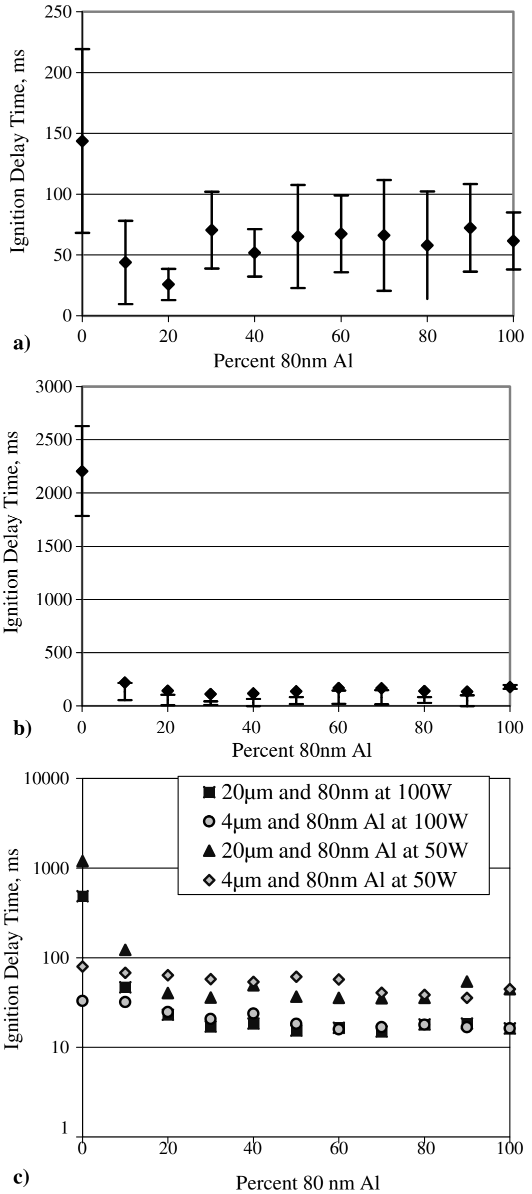

Fig. 1 Ignition time as a function of percent 80 nm Al content mixed with MoO_3 and a) 4 μm Al at 50 W laser power; b) 20 μm Al at 50 W laser power; and c) loose powders of 4 or 20 μm Al at 50 or 100 W laser power.

temperature history can be expressed as Eq. (4).

$$T_{x=0,r=0} = T_i + \frac{2q''_o\sqrt{\alpha t/\pi}}{k} \tag{4}$$

Note that the thermal properties k and α are estimated as a weighted average of the thermal properties of Al, Al_2O_3, and MoO_3. The thermal properties are also assumed to remain constant with increasing temperature. More details of this analysis are presented in [5].

Estimates of ignition temperatures were made based on experimental ignition times. Figure 2 shows four temperature history curves with the calculated and experimental ignition points, reproduced from [5]. The nano-Al composites show much lower ignition temperatures corresponding to the much lower ignition times compared with the μm Al composites. In fact, Fig. 2 suggests that the nano-Al powders ignite below 100°C and the 100% 20 μm Al mixture ignites closer to the melting point of Al (660°C).

The data suggest that if the micron-Al particles are too large (i.e., 20 μm) and only 10% nano-Al is within the composite, enough heat is lost to the larger particles to prevent a self-sustained reaction. In this case, shortly after a localized ignition spot is formed, the reaction is quenched or extinguished. Popenko et al. [1] similarly observed that if the nano-Al concentration in a mixture with micron-Al powder is less than 10%, combustion is difficult to initiate.

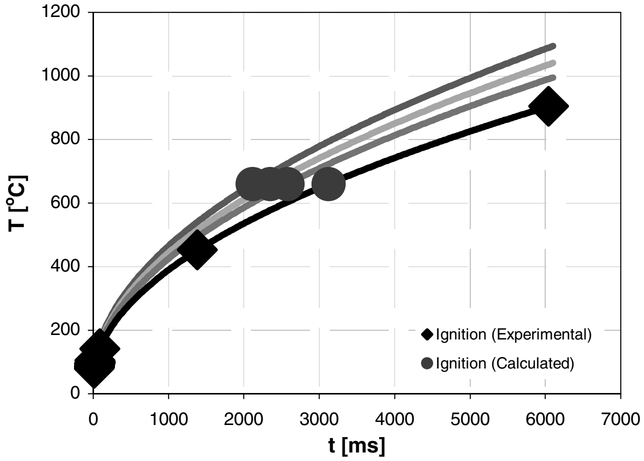

Fig. 2 Calculated temperature history from semi-infinite solid theory. Data points correspond to experimental and calculated ignition times [5].

B. Combustion Velocity

The combustion velocity as a function of 80 nm Al content is plotted in Fig. 3a for the 4 μm mixture pellet, in Fig. 3b for the 20 μm mixture pellet and Fig. 3c for the 4 and 20 μm mixture loose powders. In Fig. 3b, the data for 0 and 10% nano-Al content are not shown. In the case of 100% micron-Al, the pellet was exposed to the laser for a relatively long period of time before ignition. The exposure to this heat flux volumetrically heated the pellet, igniting the pellet under different initial thermal conditions than for the pellets containing nano-Al. Because the pellet did not ignite promptly, these data were not included. For the 10% nano-Al sample, the pellet could not sustain a self-propagating wave and velocity measurements could not be made.

The loose powder combustion velocities are plotted versus the percent nano-Al content in Fig. 3c. The piezo-electric starter was not able to ignite mixtures with 0% or 10% nano-Al content; no data are shown for these mixtures. Loose powder mixtures have different applications than pellets [4], and, for this reason, it is of interest to identify the influence of nano-Al on combustion velocity for pellets and powders.

For the combustion velocities shown in Figs. 3a–3c, the micron-Al powders appear to act as a heat sink and retard flame propagation, regardless of the micron particle size. At low densities (loose powders) the mixtures produce higher velocities because there are more convective channels through which the flame can propagate.

IV. Discussion

Figures 3a–3c show that there is a significant increase in combustion velocity with 60–70% nano-Al content for compressed pellets and loose powders. One explanation for this behavior may be related to the longer ignition delay times of the micron-Al particles. Because the micron particles require more time to ignite, the nano-Al reactions may proceed too quickly to allow the micron-Al particles to participate in the reaction. In this way, reactants containing large amounts of micron-Al particles may experience significant incomplete combustion which would result in reduced combustion velocities.

For mixtures with mostly nano-Al particles (70–90% nano-Al), the micron-Al particles make up a significantly smaller portion of the volume and impede the nano-Al + MoO_3 reaction much less. Channels of nano-Al and MoO_3 exist throughout the powder or pellet, allowing the reaction to propagate without micron-Al obstructions hindering the velocity. These channels allow the measured velocity to be the same as a mixture of pure nano-Al +

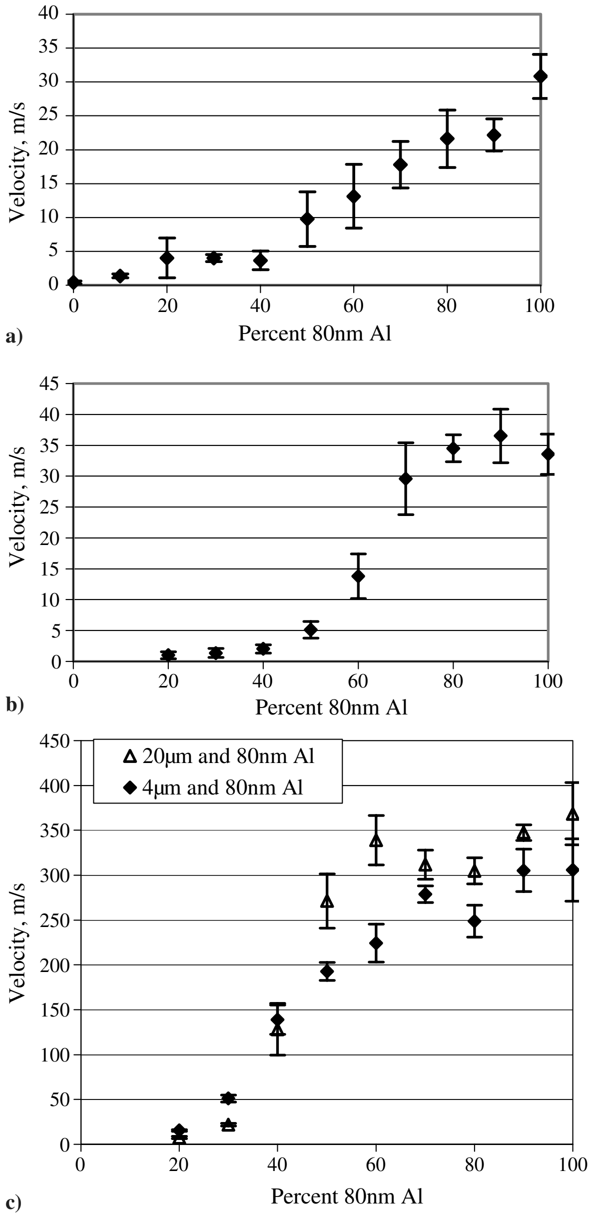

Fig. 3 Combustion velocity as a function of percent 80 nm Al content for a) pellets with 4 μm Al and MoO_3; b) pellets with 20 μm Al and MoO_3; and c) loose powder with 4 or 20 μm Al and MoO_3.

MoO_3 but may still result in incomplete reactions between micron-Al and MoO_3.

To test the hypothesis that incomplete combustion is responsible for the reduced velocities, several series of tests were performed including 1) a series of pressure measurements using the pressure cell, and 2) photographic data were collected from reacting powder samples. Figure 4 shows the peak pressure of all Al and MoO_3 loose powder mixtures as a function of percent nano-Al content. The pressure is displayed on a per unit mass basis because a slight pore density change occurred as the size distribution of the aluminum particles changed. The constant volume sample cup holds more material if composed of the more dense micron particles. The sample amount slightly increased as a result, but more important, the volume of the pressure vessel remained constant. No data points exist for the 0–20% nano-Al content due to the difficulty of igniting the mixture with the YAG laser.

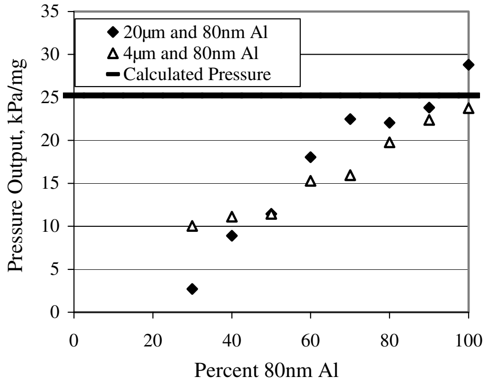

Fig. 4 Pressure output as a function of percent nano-Al content.

The maximum peak pressure of the powder samples increases as the amount of nano-Al in each mixture increases (Fig. 4). The pressure increase corresponds linearly to the increase in nano-Al content. This trend suggests that the micron-Al particles do not contribute to raising the peak pressure. For example, assuming a complete reaction between all Al particles and MoO_3, the maximum peak pressure for the mixture can be calculated assuming the peak pressure results from the rapid expansion of high temperature gasses present in the parr-bomb chamber under roughly adiabatic flame temperature conditions. Equation (5) is the ideal gas law, which assumes that the gas behavior at the flame temperature is ideal.

$$P = \frac{nRT}{V} \tag{5}$$

In this equation, P is the peak pressure and T is evaluated at the adiabatic flame temperature of the mixture 3200°C [11], which is sufficiently high enough to consider an ideal gas assumption. R is the ideal gas constant and the volume V of the combustion chamber is 9.26 cm^3. The number of moles n of gas present in the chamber is estimated based on [11] which states that 24% of the products of this reaction are gaseous at the adiabatic flame temperature. From this calculation the maximum peak pressure for a complete reaction is 25.2 kPa/mg, and is shown in Fig. 3 as the dashed line. The measured peak pressures approach 25.2 kPa/mg only when a significant percent of nano-Al is included in the mixture, indicating that the20 μm Al particles may not be contributing to fast reaction processes that produce the high peak pressures, and the pressure created by their slower heat release rate will also be lower due to more heat loss. It is noted that for the case with 100% nano-Al mixed with MoO_3, the two data points have a roughly 5 kPa/mg deviation such that an uncertainty in the measurements may be on that order. This uncertainty combined with the contribution of Al oxidation with air in the cell chamber may contribute to the measurement that exceeds the idealized calculation.

Still frame images and light traces captured during powder ignition experiments also complement the hypothesis that micron-scale particles are either not participating in the reaction or react much slower than the reaction between nano-Al and MoO_3. Figure 5a shows that for 100% nano-Al mixtures the reaction appears to consume all particles, which rise into the air and convectively cool as smoke. More important, all of the particles seem to react at the same time. A different looking reaction appears with bimodal mixtures (Fig. 5b). Initially a convective plume appears likely resulting from the nano-Al and MoO_3 reaction. The micron-Al particles may begin reacting during the nano-Al reaction with MoO_3 but appear forced into the air while still radiating and reacting. These radiating particles appear to burn much slower and are apparent even after the nano-Al plume has disappeared.

The results obtained for bimodal mixtures in a thermite composite are similar to results of bimodal Al mixtures reacting with air [1]. Popenko et al. [1] suggest incomplete combustion for nano-Al concentrations less than 20%. This finding is consistent with the slower reacting (or incomplete combustion) micron-Al particles observed in this study. Also, Dokhan et al. [3] showed a plateau in burning performance for 70% nano-Al concentration in bimodal Al mixtures added to AP. Our work shows that 70% nano-Al concentration will achieve high velocities but that combustion is incomplete for any bimodal Al distribution.

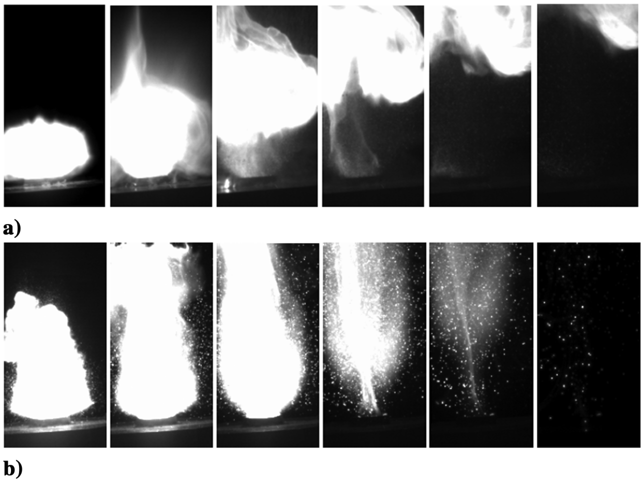

Fig. 5 a) Photographic data of 100% 80 nm Al reacting with MoO_3 as a loose powder mixture; b) photographic data of 10% 80 nm Al and 90% 20 μm Al reacting with MoO_3 as a loose powder mixture.

The most meaningful reaction parameter from these results is the suggestion of incomplete or delayed combustion of the micron-scale powders. This finding could impact the use of a bimodal composite by showing that the reaction efficiency is poor because micron-scale particles are not participating in the primary reaction. The results presented here may also have implications towards the use and handling of thermites. Nano-scale Al particles can be costly, significantly more so than micron-scale particles. It may be advantageous to use mixtures of nano- and micron-scale material for large scale formulations. This work shows that ignition sensitivity is heightened by small additions of nano-Al to the mixture. However, what is gained in ignition sensitivity is sacrificed in performance through reduced velocities that result from incomplete (or significantly slower) micron-Al oxidation.

V. Conclusions

The ignition delay time and combustion velocity of thermite composites composed of $Al + MoO_3$ were examined as a function of Al particle size distribution. Bimodal Al size distributions consisting of 80 nm combined with either 4 or 20 μm Al particles showed increased sensitivity to ignition with only a 10% concentration of nano-Al. However, the benefit of a reduced ignition delay time with added nano-Al can also be achieved simply by using fine (4 μm) Al particles. It was also shown that using 20 μm Al and less than 20% nano-Al resulted in a quenched reaction. In this case, heat is lost to the surrounding media too quickly to permit a sustained reaction. Overall, at least 20% nano-Al particles are required to ensure reduced ignition delay times that are on the same order as mixtures containing 100% nano-Al.

The combustion velocity increases linearly with nano-Al content from roughly 1 to 40 m/s (pellets) to 300 m/s (powders). Slow (and incomplete) combustion of micron-Al particles leads to decreased combustion velocities for mixtures with high micron-Al content. This observation was confirmed through pressure cell measurements and high-speed video observations of loose powder reactions. For mixtures with small amounts of micron-Al, the reaction speed is significantly increased because the nano-Al can react with MoO_3 in channels that exist around the micron-Al particle obstacles.

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