The effect of pre-heating on flame propagation in nanocomposite thermites

Birce Dikici a, Michelle L. Pantoyaa,*, Valery Levitas b

a Mechanical Engineering Department, Texas Tech University, Lubbock, TX 79409, USA
b Departments of Mechanical Engineering, Aerospace Engineering, and Material Science and Engineering, Iowa State University, Ames, IA 50011, USA

1. Introduction

Thermite reaction is a chemical reaction in which a metallic fuel (i.e., Al) is oxidized by a metal oxide (MoO3, CuO, NiO). Exothermic heat release from the reaction is quantified by the enthalpy of combustion ($D_{\text{H}}$) which is defined as the enthalpy change from the reactants to the products. Enthalpy of combustion is affected by parameters that include temperature, pressure, stoichiometry and reactant surface area. Any of these factors can change the number of collisions between molecules as well as the probability that a collision will result in reaction.

Experiments were performed in a semi-confined flame tube apparatus housed in a reaction chamber initially at standard atmospheric pressure. The flame propagation behavior for the nano-particle thermite was compared to micron particle thermite of the same composition. Results indicate that increasing the initial temperature of the reactants results in dramatically increased flame speeds for nanocomposite thermite (i.e., from 627 to 1002 m/s for ambient and 105 °C pre-heat temperature, respectively) and for micron composite thermite (i.e., from 205 to 347 m/s for ambient and 170 °C pre-heat temperature, respectively) samples. Experimental studies were extended giving a cooling time for the heated thermites prior to ignition and flame propagation. It is shown that when 105 °C and 170 °C pre-heated thermites are cooled at a rate of 0.06 K/s, almost the same flame speeds are obtained as thermites at ambient temperature. However, when the cooling rate is increased to 0.13 K/s, the measured flame speeds approach the flame speeds of pre-heated samples.

© 2010 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Flame propagation in a confined tube configuration was evaluated for aluminum (Al) and molybdenum trioxide (MoO3) thermites starting at room temperature and pre-heated up to 170 °C. Flame propagation was analyzed via high speed imaging diagnostics and temperatures were monitored with thermocouples. Experiments were performed in a semi-confined flame tube apparatus housed in a reaction chamber initially at standard atmospheric pressure. The flame propagation behavior for the nano-particle thermite was compared to micron particle thermite of the same composition. Results indicate that increasing the initial temperature of the reactants results in dramatically increased flame speeds for nanocomposite thermite (i.e., from 627 to 1002 m/s for ambient and 105 °C pre-heat temperature, respectively) and for micron composite thermite (i.e., from 205 to 347 m/s for ambient and 170 °C pre-heat temperature, respectively) samples. Experimental studies were extended giving a cooling time for the heated thermites prior to ignition and flame propagation. It is shown that when 105 °C and 170 °C pre-heated thermites are cooled at a rate of 0.06 K/s, almost the same flame speeds are obtained as thermites at ambient temperature. However, when the cooling rate is increased to 0.13 K/s, the measured flame speeds approach the flame speeds of pre-heated samples.

© 2010 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Flame propagation in a confined tube configuration was evaluated for aluminum (Al) and molybdenum trioxide (MoO3) thermites starting at room temperature and pre-heated up to 170 °C. Flame propagation was analyzed via high speed imaging diagnostics and temperatures were monitored with thermocouples. Experiments were performed in a semi-confined flame tube apparatus housed in a reaction chamber initially at standard atmospheric pressure. The flame propagation behavior for the nano-particle thermite was compared to micron particle thermite of the same composition. Results indicate that increasing the initial temperature of the reactants results in dramatically increased flame speeds for nanocomposite thermite (i.e., from 627 to 1002 m/s for ambient and 105 °C pre-heat temperature, respectively) and for micron composite thermite (i.e., from 205 to 347 m/s for ambient and 170 °C pre-heat temperature, respectively) samples. Experimental studies were extended giving a cooling time for the heated thermites prior to ignition and flame propagation. It is shown that when 105 °C and 170 °C pre-heated thermites are cooled at a rate of 0.06 K/s, almost the same flame speeds are obtained as thermites at ambient temperature. However, when the cooling rate is increased to 0.13 K/s, the measured flame speeds approach the flame speeds of pre-heated samples.

© 2010 The Combustion Institute. Published by Elsevier Inc. All rights reserved.
temperature. For example, in hydrocarbon combustion, hot air at 600 K increases the adiabatic flame temperature by 150 K (7.1%) compared to the ambient air case [2]. Air pre-heating also affects the combustion characteristics by changing the heat generation, heat transfer and reaction rates [5]. Zhau et al. [5] investigated the effect of initial reactant temperature on the combustion characteristics of corn straw with air. In their study, increasing the initial temperature of the air increased the average propagation rate from 1.63 m/h at 20°C to 2.84 m/h at 130°C. Higher initial air temperature also shortened the total burning time and produced a lower ignition front flame temperature [5].

Granier and Pantoya [1] investigated combustion behaviors of pre-heated nanocomposite thermites composed as pellets. They pre-heated Al/MoO₃ pellets with a 50 W laser before ignition. Ignition delay time decreased and the propagation rate increased with elevated initial sample temperatures. The ignition times dropped from 0.066 to 0.006 s and the propagation rates increased from 21.5 to 61.6 m/s for 20–200 °C pre-heat temperatures, respectively [1].

Granier and Pantoya [1] also effectively altered the reactant temperature of a consolidated thermite by using variable laser power. Using powders pressed into cylindrical pellets, Granier and Pantoya showed that by controlling the laser power prior to ignition they could control the conductive heating through reactant composite and generate higher reactant temperatures prior to ignition. Once ignited, the pellets at higher initial temperatures demonstrated roughly 20% higher flame propagation rates [1].

The present study investigates the effect of pre-heating on flame propagation of micron versus nanometric aluminum particles combined with molybdenum trioxide particles as loose powders ignited in confined tube configuration. For this reason, individual mixtures of 3–4.5 μm Al + MoO₃ and 80 nm Al + MoO₃ are ignited under varying initial temperatures and flame propagation rates are compared. A semi-confined flame tube apparatus was used to investigate flame propagation. This system is commonly used to examine flame propagation behavior in solid materials such as thermites [6–8] because it allows visual observation of the reaction wave and can be instrumented to monitor temperature and pressure histories. The flame tube apparatus used here was modified such that the reactants could be pre-heated to elevated temperatures. Based on the ease of reactant preparation, data collection and control over reactant conditions, the flame tube apparatus was selected as diagnostic for this study.

### 2. Experimental

#### 2.1. Sample preparation

Two different Al samples were studied. Physical property information for the particles is listed in Table 1. The nano Al sample was purchased from Nanotechnologies with an average particle diameter of 80 nm and the micron-Al sample was purchased from Alfa

| Table 1
<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer</th>
<th>Particle size</th>
<th>Oxide thickness (nm)</th>
<th>Active Al (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-nano</td>
<td>NovaCentrix</td>
<td>80 nm</td>
<td>4</td>
<td>80</td>
</tr>
<tr>
<td>Al-micron</td>
<td>Alfa Aesar</td>
<td>3–4.5 μm</td>
<td>2</td>
<td>97.5</td>
</tr>
<tr>
<td>MoO₃</td>
<td>NovaCentrix</td>
<td>44 nm</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Aesar with an average diameter of 3–4.5 μm (provided by the manufacturer and confirmed via scanning electron microscope (SEM) images). Both Al-nano and Al-micron have a spherical morphology. Each Al was combined with nano-scale MoO₃ which has a rod-like morphology and was purchased from Nanotechnologies. Note that for the Al-nano, the active Al content refers to Al that is not in the form of Al₂O₃.

#### 2.2. Procedure

For both particle sizes of Al, the Al and MoO₃ samples were mixed at an equivalence ratio (ER) 1.2. This equivalence ratio produced the highest speeds for Al–MoO₃ in the previous tests [6,9]. To combine reactants, the mixtures are suspended in hexane and ultrasonic waves are applied to ensure a more homogeneous mixture. A Misonix Sonicator 3000 probe vibrating at ultrasonic speeds is used to improve mixing by breaking up agglomerates. This device is programmed to produce ultrasonic waves for 60 s with 10 s on/off intervals. Each 10 s interval prevents a temperature increase and possible thermal damage to the sample. The mixtures are poured into a Pyrex container to evaporate the hexane. After the evaporation, the powder is reclaimed for experimentation.

Once prepared the powder mixture is placed into a quartz tube shown in Fig. 1 while in a glove box with a controlled, well-dried inert argon environment. Within the glove box, the powder filled tube is placed onto a vibrating block for 5 s to reduce density gradients, after which more powder is added. This process results in a loose powder mixture with a bulk density of 8% of the theoretical maximum density (TMD). In this case, TMD is calculated as the ratio of the actual mass of reactants divided by sample volume to the weighted average of pure solid densities of each reactant. The tube is sealed at both ends with electrical tape and one end also secures the nichrome wire ignition source. The tube is placed into the steel testing block designed with viewing windows to image the quartz tube. The transparency of quartz enables viewing the flame propagation inside the tube during combustion.

A coiled heater inserted around the steel block heats the thermit powder uniformly (Fig. 2). The coiled heater includes a J-type thermocouple which monitors the heater temperature. A K-type thermocouple embedded in the powder and positioned in the tube at half the distance from the ignition source (i.e., roughly 50 mm from the end) measures the powder temperature. The coiled heater has a heating rate of 16 °C/s which provides a powder heating rate
of 0.134 °C/s. Once the thermite powder reached the specified preheat temperature, the coiled heater was removed. The mixture was ignited and flame propagation measured using high speed imaging diagnostics. The delay including heater removal to ignition is estimated as 6 s such that there is no significant cooling of the powder prior to the experiment.

The steel test block with the coiled heater apparatus is housed inside a stainless steel combustion chamber for safety purposes. The combustion chamber has an acrylic window (139.7 × 25.4 mm dimensions) which enables imaging of the reaction. The product gases are vented from the chamber during and after the reaction. All experiments were performed in the stainless steel chamber at 1 atm pressure in an air environment.

A Vision Research Phantom 7.1 high-speed camera was positioned perpendicular to the direction of flame propagation and used to record flame propagation rates. The monochromatic camera captures visible light at 51,000 frames per second (fps). This frame rate allowed a 16 s temporal resolution between images. The rate was measured with the high-speed camera and imaging software. The Vision Research software provided with the Phantom IV camera provides a means of post processing video data. By establishing a reference length, the software determines speed based on a distance between sequential time frames. Using a “find edge” image filter that identifies pre-set variations in pixel intensity, the highly luminescent flame front location is identified and marked for speed measurements.

Six different flame propagation tests were performed. In this assembly, the limiting resistance to heat diffusivity through the powder is the steel block, which has a thickness of less than 1 cm. The characteristic time for heat diffusion through the steel block can be calculated as the characteristic length in the heat flow direction (radial direction) squared divided by the thermal diffusivity of the limiting material (i.e., \( \tau = L^2/\alpha \)). Conservatively, \( L \) is estimated as 1 cm and the thermal diffusivity of steel is \( 17.7 \times 10^{-6} \text{ m}^2/\text{s} \) such that \( \tau = 565 \text{ s} \) (or 9.4 min). Therefore, it is assumed that thermal equilibrium is reached after 10 min of holding at elevated temperature because this gives time for more homogenous temperature distribution. This holding time also gives time for any changes (removing of impurities, relaxation processes, and agglomeration) that potentially occur.

**Test 1**: The initial powder temperature corresponds to: 25, 80, 105, 145 and 170 °C, respectively. For these tests the samples are designated 25, 80, 105, 145, and 170.

**Test 2**: The thermite powder was pre-heated to 105 °C and thermal equilibrium (TE) conditions were assumed after 10 min held at 105 °C. For this test the sample is designated 105TE.
Test 3: The thermite powder was pre-heated to 170 °C and TE conditions were assumed after 10 min held at 170 °C. For this test the sample is designated 170TE.

It is noted that for the 105 and 170 samples, thermal equilibrium may not have been reached within the powder; but, for the 105TE and 170TE samples, thermal equilibrium within the powder is assumed.

Test 4: The thermite powder was pre-heated to 105 °C, TE conditions were achieved after 10 min and the thermite was cooled to 25 °C at a cooling rate (CR) of 0.06 °C/s or 0.13 °C/s, respectively. These samples are designated as 105TE25CR06 and 105TE25CR13, respectively.

Test 5: The thermite powder was pre-heated to 170 °C, TE conditions were achieved after 10 min and the thermite was cooled to 25 °C at a cooling rate (CR) of 0.06 °C/s or 0.13 °C/s, respectively. These samples are designated as 170TE25CR06 and 170TE25CR13, respectively.

3. Results

Table 2 shows the velocity measurements for micron Al + MoO3 and nano Al + MoO3 samples for the different test temperatures. Fig. 3 summarizes the data presented in Table 2. The uncertainty in Table 2 and error bars shown in Fig. 3 are calculated from the sample standard deviation $\sigma(x)$ and standard error of the mean ($\sigma_x$) from the following equations:

$$\sigma(x) = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (x_i - \bar{x})^2}, \quad \sigma_x = \frac{\sigma}{\sqrt{N}}$$

where $N$ is the number of experiments and $\bar{x}$ is the mean measured flame speed for three repeatability tests. Therefore, $2\sigma_x$ represent the width of each error bar. Variations in the repeatability of the data may be attributed to a variety of parameters including density gradients, particle size distributions, passivation shell thickness variations, agglomeration of particles, mixture homogeneity, concentration gradients.

The cooling rate after pre-heating to 105 °C was increased further to 0.33 °C/s. This was done by rapidly quenching the pre-heated powders by placing them into an ice bed prior to insertion within the combustion chamber. This treatment caused spontaneous ignition such that the mixture ignited upon any contact or movement involving the powder and should be avoided as a safety hazard. No flame speed data could be obtained in this case due to the high reactivity of the powder.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Velocity (m/s)</th>
<th>Micron</th>
<th>Nano</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>205 ± 6</td>
<td>627 ± 19</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>300 ± 99</td>
<td>910 ± 45</td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>330 ± 17</td>
<td>1002 ± 60</td>
<td></td>
</tr>
<tr>
<td>145</td>
<td>310 ± 16</td>
<td>986 ± 49</td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>315 ± 16</td>
<td>960 ± 67</td>
<td></td>
</tr>
<tr>
<td>Test 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>105TE</td>
<td>343 ± 3</td>
<td>909 ± 45</td>
<td></td>
</tr>
<tr>
<td>Test 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>170TE</td>
<td>347 ± 10</td>
<td>948 ± 47</td>
<td></td>
</tr>
<tr>
<td>Test 4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>105TE25CR06</td>
<td>223 ± 11</td>
<td>631 ± 32</td>
<td></td>
</tr>
<tr>
<td>105TE25CR13</td>
<td>290 ± 6</td>
<td>820 ± 32</td>
<td></td>
</tr>
<tr>
<td>Test 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>170TE25CR06</td>
<td>226 ± 7</td>
<td>641 ± 32</td>
<td></td>
</tr>
<tr>
<td>170TE25CR13</td>
<td>214 ± 11</td>
<td>737 ± 37</td>
<td></td>
</tr>
</tbody>
</table>

4. Discussion

Fig. 3 shows that for both Al particle sizes, pre-heating the thermite to 105 °C correspondingly increases the flame propagation rate. For nanoparticles, at temperatures in excess of 105 °C, the average propagation rate increases slightly then decreases with the range for these pre-heated samples between 895 and 1055 m/s; considerably greater than the 600–650 m/s range associated with non-pre-heated samples. The decrease in average propagation rate may be attributed to sintered or agglomerated particles that counterbalance the effect of smaller particle size. For micron particles, increasing the pre-heat temperature to 170 °C correspondingly increases the propagation rate. There are two mechanisms that may affect flame speed at elevated initial temperatures. First, increasing the reactant temperature increases the kinetic rate of the reaction. Another possibility may be related to chemical impurities within the particle reactants that are removed upon pre-heating. Specifically, bonded water (–OH) has been reported in other studies to affect thermite performance [10]. For this reason, the thermite powders were pre-heated and then allowed to cool to ambient temperature prior to ignition and self propagation (i.e., Tests 4 and 5). In this way, the influence of removal of chemical impurities on the flame propagation can be assessed. As shown in Table 2 and Fig. 3 for Test 4, when 105 °C heated powders are cooled, the propagation rate is almost the same as measured for the 25 °C particles. These results imply that the increased propagation rates are related to the thermal effect of the pre-heating more directly than the influence of chemical impurities that may have been removed upon pre-heating. A similar test and result was found for the thermite powders pre-heated to 170 °C and cooled to ambient (i.e., Test 5).
For the set of tests that established thermal equilibrium (i.e., Tests 2 and 3), results showed that nanoparticles demonstrate lower flame propagation rates (9.29% lower at 105 °C and 1.25% lower at 170 °C), whereas micron particles showed higher rates (3.93% higher at 105 °C and 10.15% higher at 170 °C), after thermal equilibrium comparing to not reaching thermal equilibrium cases (Test 1).

For Tests 4 and 5, ignition upon cooling (from 105 °C and 170 °C) showed that thermite flame propagation rates approached the rates obtained for the pre-heated case as the cooling rates are increased from 0.06 °C/s to 0.12 °C/s. These measurements show that regardless of Al particle size, as the cooling rate is increased, the propagation rates of the cooled powder are roughly the same as the pre-heated powder. This is an indication that the physical state of the reactant particles has been changed by manipulating the particles' thermal pre-history. This result will be interpreted further for its implications toward creating a pre-stressed state of the reactant particle and how that pre-stressed condition impacts the particles' mechanism of reaction [11–13].

Although the impact of pre-heating on thermite reactions has not been studied, pre-heating of hydrocarbon flames has been studied extensively. Fristrom and Westenberg [14] showed the flame speed as a function of temperature for 10% H2–air mixture. When the pre-heat temperature is brought from 298 to 473 K, the flame speed increased from 17 to 67 cm/s (i.e., 294.1% increase). Ogami and Kobayashi [15] studied the flame speed of stoichiometric CH4/air premixed flames. When the initial temperature was brought from 298 to 400 K, the flame speed increased from 35 to 55 cm/s (i.e., 51.7% increase). As a baseline, these two studies suggest that mildly energetic mixtures (i.e., H2–air) may exhibit greater increases in flame speed with increased initial temperature than more energetic mixtures (i.e., CH4–air). For an even smaller pre-heat temperature range studied here (i.e., 390–450 K), the increase in flame speed with temperature is on the order of 60% for nanometric and 70% for micron scale mixtures and is suggestive of alteration of chemical and physical properties of the reactants.

5. Conclusion

Effects of thermite powder pre-heating on flame propagation rates are studied for micron and nano Al with Mo03. Similar trends are found for micron and nano Al particles. For nano Al, pre-heating leads to a 60% higher propagation rates compared to non-pre-heating. For micron Al pre-heating leads to 70% higher propagation rates compared to non-pre-heating. Pre-heating the sample prior to ignition increases reaction heat and enhances the flame propagation rates.

When pre-heated thermites are cooled slowly, almost the same flame propagation rates are obtained as thermites at ambient temperature. However, when the cooling rate is increased from 0.06 to 0.13 °C/s, the measured flame rates approach the rates of pre-heated samples. These results imply that the Al particles are physically altered by pre-heating and rapid cooling such that the particle's reactivity is increased.

Acknowledgments

The authors gratefully acknowledge support from the Army Research Office contract W911NF-04-1-0217 [program director Dr. Ralph Anthenien], Office of Naval Research contract N000140810104 (program director Dr. Clifford Bedford), and National Science Foundation grant CBET-0755236.

References