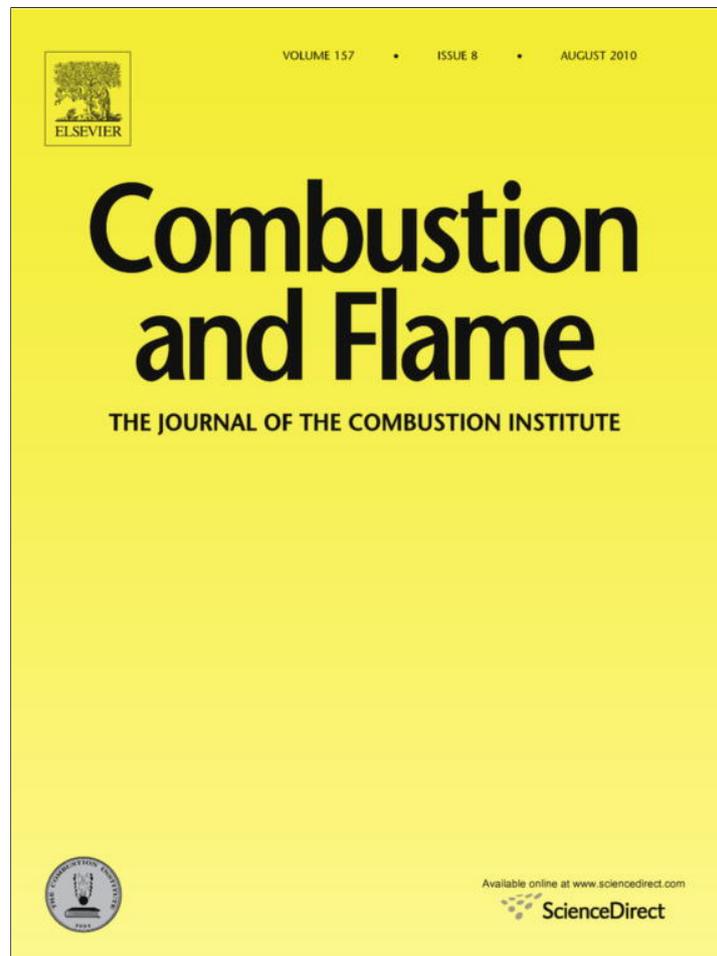


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

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

Birce Dikici^a, Michelle L. Pantoya^{a,*}, 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

ARTICLE INFO

Article history:

Received 9 October 2009

Received in revised form 13 January 2010

Accepted 14 April 2010

Available online 11 May 2010

Keywords:

Thermites

Aluminum combustion

Flame speeds

Nanoparticles

Reaction propagation

Energetic material combustion

ABSTRACT

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.

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 (ΔH_c) 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.

Examining a reaction at high initial temperatures and at subsequent cooling allows interpretation of how the flame propagation behavior may be influenced by thermal pre-history. Pre-heating and cooling may be conditions that increase particle reactivity and the effect of pre-heating and cooling on performance and safety should be evaluated. While there are limited studies on thermite pre-heating of compressed pellets [1], there is no reporting in the literature of the influence of pre-heating on powder thermites. We present here an exploratory experimental study that sheds light on this topic. In a similar way as traditional gas phase combustion [2], pre-heating may influence flame propagation through (i) reducing ignition time; (ii) increasing enthalpy of reactants; (iii)

increasing adiabatic flame temperature; and (iv) changing physical and chemical states of the particles (unique to particle laden flames). As the initial temperature of the mixture increases, the overall flame propagation rate should increase accordingly. One of the objectives of this study is to understand the correlation between pre-heat temperature and flame propagation rate in powder thermite reactions.

For observing the pre-heating temperature on the flame front propagation rate and degree of conversion from reactants to products, Yeh et al. [3] performed self-propagating high temperature synthesis (SHS) of tantalum nitride with tantalum compacts in nitrogen. The conversion was increased by 15% compared with no pre-heating when sample initial temperature increased from 25 to 150 °C. However, further increases in initial temperature up to 300 °C did not additionally increase the degree of conversion. Pre-heating the sample prior to combustion caused higher combustion temperatures and led to higher flame propagation rates and conversion percentage [3]. Yeh et al. [4], performed experiments with vanadium powder compacts in gaseous nitrogen to observe the effects of pre-heating on SHS of vanadium nitride (VN). Their study showed that sample reaction propagation rates increased around 16% by pre-heating the reactant powder up to 200 °C [4].

Another technique to pre-heat reactants involves pre-heated combustion air used in fuel fired industrial heating processes. Pre-heated air is generally used because it elevates the flame

* Corresponding author.

E-mail address: michelle.pantoya@ttu.edu (M.L. Pantoya).

Nomenclature

ΔH_c	enthalpy of combustion	m_{MoO_3}	mass of MoO_3
Φ	equivalence ratio	T_{af}	the adiabatic flame temperature
F	mass of fuel	h_f^o	enthalpy of forming
O	mass of the oxidizer	c_p	constant specific heats
p_{Al}	purity of Al	N	mole number
p_{MoO_3}	purity of MoO_3	H_{react}	enthalpy of reactants
m_{Al}	mass of Al	H_{prod}	enthalpy of products
$m_{\text{Al}_2\text{O}_3}$	mass of Al_2O_3		

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 compressed as pellets. They pre-heated Al/ MoO_3 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 + MoO_3 and 80 nm Al + MoO_3 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
Material properties of reactant powders.

Material	Manufacturer	Particle size	Oxide thickness (nm)	Active Al (%)
Al-nano	NovaCentrix	80 nm	4	80
Al-micron	Alfa Aesar	3–4.5 μm	2	97.5
MoO_3	NovaCentrix	44 nm	–	–

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 MoO_3 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 Al_2O_3 .

2.2. Procedure

For both particle sizes of Al, the Al and MoO_3 samples were mixed at an equivalence ratio (ER) 1.2. This equivalence ratio produced the highest speeds for Al– MoO_3 in the previous tests [6,9]. To combine reactants, the mixtures are suspended in hexane and ultrasonic waves are applied to ensure a more homogenous 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 tubes. The transparency of quartz enables viewing the flame propagation inside the tube during combustion.

A coiled heater inserted around the steel block heats the thermite 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

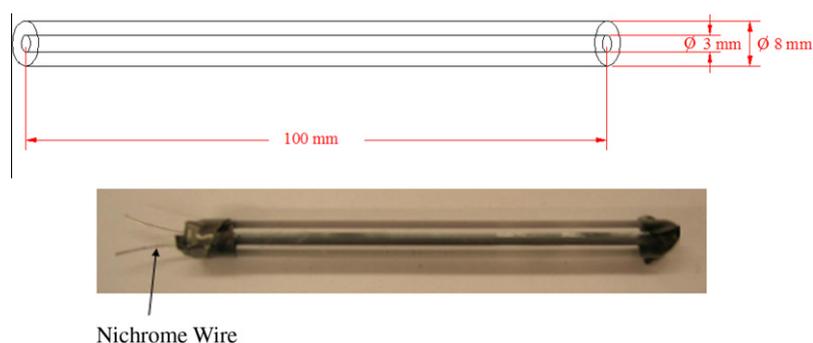


Fig. 1. Schematic diagram illustrating the quartz tube used for flame speed measurements.

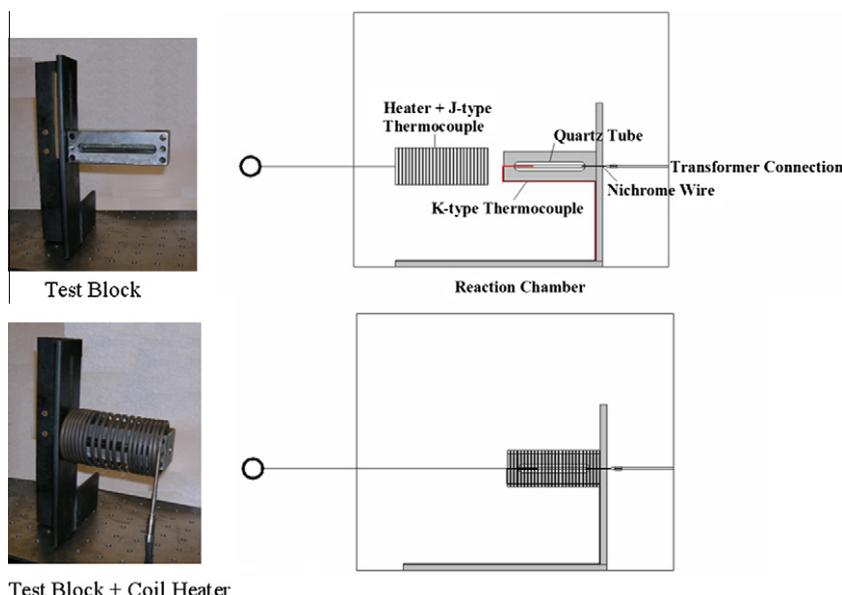


Fig. 2. Photographs and schematic diagrams illustrating the tube, test block and coiled heater. In schematic the nichrome wire is used for ignition, the J-type thermocouple monitors the heater temperature and the K-type thermocouple monitors powder temperature. Bottom schematic illustrates coil heater surrounding test block.

of 0.134 °C/s. Once the thermite powder reached the specified pre-heat 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 inten-

sity, 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 power 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 $\sigma(\bar{x})$ and standard error of the mean (σ_x) from the following equations:

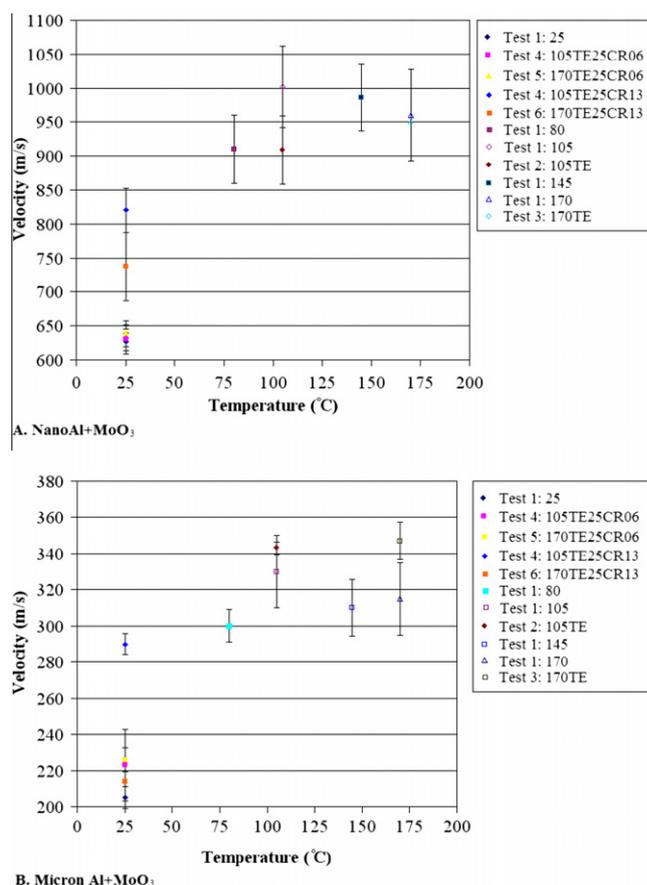
$$\sigma(\bar{x}) = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2}, \quad \sigma_x = \frac{\sigma}{\sqrt{N}}$$

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
Summary of flame propagation results.

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



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., a 57.1% 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 MoO₃. 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

- [1] J.J. Granier, M.L. Pantoya, American Institute of Aeronautics and Astronautics, in: Conference Proceedings of the AIAA Meeting, Reno, NV, 2005.
- [2] S.R. Turns, An Introduction to Combustion, second ed., Mc Graw Hill Co., New York, 2000. pp. 32–66.
- [3] C.L. Yeh, E.W. Liu, Y.C. Chang, J. Eur. Ceram. Soc. 24 (4) (2004) 3807–3815.
- [4] C.L. Yeh, H.C. Chuang, E.W. Liu, Y.C. Chang, Ceram. Int. (2004).
- [5] W. Zhou, L. Zhengqi, G. Zhao, F. Zhang, Q. Zhu, Elsevier, 2008.
- [6] B.S. Bockmon, M.L. Pantoya, S.F. Son, B.W. Asay, J.T. Mang, Combustion velocities and propagation mechanisms of meta-stable intermolecular composites, J. Appl. Phys. 98 (6) (2005) 064903, doi:10.1063/1.2058175.
- [7] M.R. Weismiller, J.Y. Malchi, R.A. Yetter, T.J. Foley, Dependence of flame propagation on pressure and pressurizing gas for an Al/CuO nanoscale thermite, Proc. Combust. Inst. 32 (2009) 1895–1903.
- [8] J.Y. Malchi, R.A. Yetter, T.J. Foley, S.F. Son, The effect of added alumina on the propagation behavior of an Al/CuO nanoscale thermite, Combust. Sci. Technol. 180 (7) (2008) 1278–1294.
- [9] J.J. Granier, M.L. Pantoya, Combust. Flame 138 (4) (2004) 373–383.
- [10] J.J. Granier, K.B. Plantier, M.L. Pantoya, J. Mater. Sci. 39 (4) (2004) 6421–6431.
- [11] V.I. Levitas, B.W. Asay, S.F. Son, M. Pantoya, J. Appl. Phys. 101 (2007) 083524.
- [12] V.I. Levitas, M.L. Pantoya, B. Dikici, Appl. Phys. Lett. 92 (2008) 011921.
- [13] V.I. Levitas, M. Pantoya, K.W. Watson, Appl. Phys. Lett. 92 (2008) 201917.
- [14] R.M. Fristrom, A.A. Westenberg, Flame Structure, Mc Graw Hill, New York, 1965.
- [15] Y. Ogami, H. Kobayashi, Laminar burning velocity of stoichiometric CH₄/air premixed flames at high pressure and high temperature, JSME Int. J. Ser. B 48 (3) (2005) 603–700.