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THERMITE COMBUSTION ENHANCEMENT RESULTING FROM BIMODAL ALUMINUM DISTRIBUTION

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Abstract

In recent years many studies that incorporated nano-scale or ultrafine aluminum (Al) as part of an energetic formulation and demonstrated significant performance enhancement. Decreasing the fuel particle size from the micron to nanometer range alters the material's chemical and thermal-physical properties. The result is increased particle reactivity that translates to an increase in the combustion wave speed and ignition sensitivity. 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 wave speed experiments were performed using a thermite composite of Al and MoO_3 pressed to a theoretical maximum density of 50% (2 g/cm^3). A bimodal Al particle size distribution was prepared using 4 or 20 μm Al fuel particles that were replaced in 10% increments by 80 nm Al particles until the fuel was 100% 80 nm Al. These bi-modal distributions allow the unique characteristics of nano-scale materials to be better understood. The pellets were ignited using a 50W CO_2 laser. High speed imaging diagnostics were used to measure the ignition delay time and combustion wave speed.

Introduction

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

Using nanometer combined with micron scale Al particles in rocket propellant applications has strong advantages. For example, all Al particles are pyrophoric and therefore 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 nanometer to micron-scale 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 aluminum particle size distributions was examined. They showed a significant increase in burn rate with only a 20% addition of nanometer 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 may increase the temperature at the burning surface and correspondingly increase the burn rate.

Thermite reactions, 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 used to fire guns [4]. Reducing the presence of toxins such as lead in firearms will not only reduce health risks to personnel but will also improve the environment. In particular, nanometer Al mixed with molybdenum trioxide and acetylene black (a form of carbon) is being studied as a replacement for lead compounds [4].

Granier et al [5] examined the ignition and burning behavior of Al-MoO_3 composites as a function of Al particle size. Their work showed that reducing the Al particle size from micron to nanometer dimensions decreased the ignition time by two orders of magnitude (from roughly 10 s to 10 ms). The significantly enhanced ignition sensitivity may be attributed to the reduced melting temperature associated with nanometer particles [5]. On the nano-scale the ratio of surface to interior atoms is high resulting in an overall higher surface energy state than with larger size particles. This energy manifests itself in the form of increased surface tension and altered thermodynamic properties, namely a reduced melting temperature [6]. Because thermite reactions are typically diffusion controlled, the melting of one species can trigger the diffusion reaction [7]. Because the melting of nanoparticles occurs at reduced temperatures, the diffusion reaction may initiate at lower temperatures and result in shorter ignition delay times. Other factors may also contribute to the enhanced ignition sensitivity, such as altered absorption properties which enable nano-Al particles to absorbed higher concentrations of energy than their micron scale counterparts. In fact, Yang et al [8] showed that the absorption coefficient of 30-nm Al particles is significantly greater than micron scale particles and a strong function of particle size (see Fig. 5 of Ref. 8).

This study will examine the ignition sensitivity and combustion wave speed of Al – MoO_3 composites as a function of the Al size distribution. Mixtures are prepared using 4 or 20 micron combined with 80 nm diameter Al particles in discrete mixture ratios. Experiments were performed on pressed pellet samples using a laser ignition apparatus and a high speed imaging diagnostic system to record ignition and flame propagation. The goal of this study is to investigate the influence of nanometer scale Al on enhancing the ignition sensitivity and combustion wave speed of thermites.

Experimental

Sample Preparation

The aluminum was mixed with MoO_3 on a 40/60 wt % ratio which corresponds to a slightly fuel rich equivalence ratio of 1.1. This mixture ratio was shown to be an optimal composition for achieving the highest combustion wave speed and shortest ignition delay time [5]. The powders were dispersed in a hexane solution and sonicated for 20 minutes to break up agglomerates and ensure a homogeneous mixture. The wet solution was poured into a tray and slightly heated to allow hexane evaporation. A well-mixed, dried powder was separated into 230-270 mg quantities and cold pressed with a hydraulic press and a uniaxial die. All final pellets were 3.9 mm in diameter and 6.51 mm in length and pressed to a theoretical maximum density of 50% ($\approx$2 g/cc). Theoretical maximum density calculations are based on the weighted average of Al, MoO_3, and Al_2O_3 present in the mixture. Particle descriptions of each reactant are tabulated in Table 1.

Eleven mixtures of Al/MoO_3 were prepared, each with a varying distribution of aluminum size. The active Al content of each sample remained relatively constant, however, the Al particle size distribution varied from 100 % 80 nm to 100 % 4 or 20 micron. The distribution of active aluminum by particle size for each of the samples is illustrated in Figure 1. An SEM micrograph shown in Fig. 2 illustrates the relative size of the 80 nm and 4 um Al particles.

Table 1 Reactant Particle Description

Particle	% Active Al	Al2O3 Thickness	Supplier
80 nm Al	73	4.3 nm	Nanotechnologies, Inc.
4 um Al	91	70 nm	Alfa Aesar
20 um Al	99	30 nm	Sigma Aldridge
MoO3	-	-	Technanogy/Climax

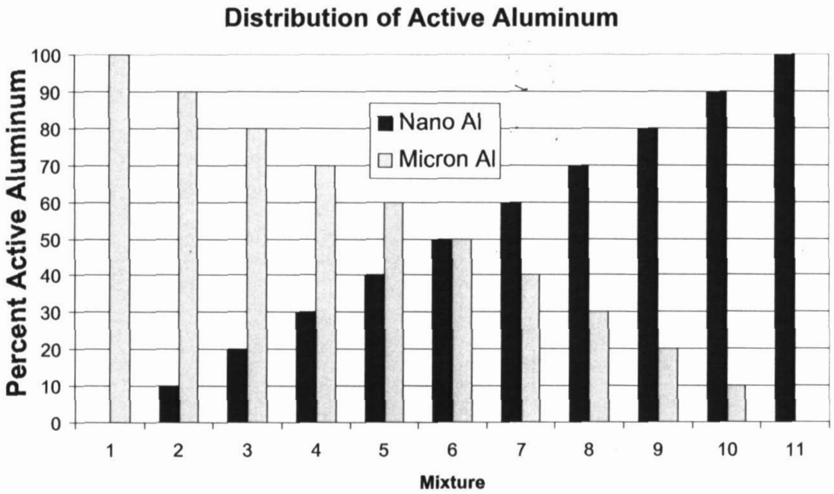


Figure 1 Schematic illustrating bimodal mixture ratios

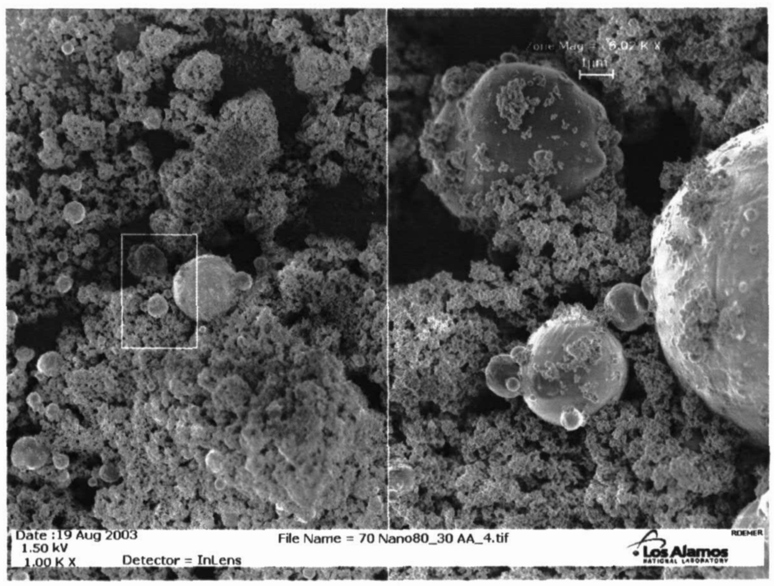


Figure 2 An SEM micrograph of an 80 nm and 4 um Al mixture

Experimental Setup

The laser ignition apparatus consists of a 50-W CO2 laser, power meter and associated optics. A complete description of this apparatus is presented in [5] but will be summarized here for completeness. The laser beam and pellet diameter are equal such that the flat surface of the cylindrical pellet was aligned with the laser beam. In this way, the slight Gaussian distribution of laser energy causes the pellet center to ignite first. A Phantom IV high speed camera captured images of the reaction at 32,000 frames per second.

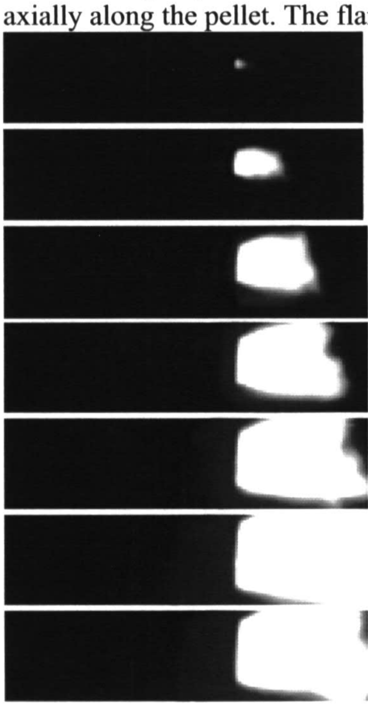
Ignition is defined in the context of thermite combustion as the onset of a fully sustained self-propagating reaction. If the reaction is extinguished or quenched before consuming all reactants, the sample was deemed not to have achieved ignition. There are several techniques for measuring an ignition 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 and detection of the first light. This may not guarantee ignition but is a commonly used technique for experimentally determining ignition times [9]. 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.

Burn rate is a measure of the burning solid surface of an energetic material and often is used in reference to a single particle. Propellant combustion studies typically refer to a mass burning rate which characterizes the regression rate of the combusting solid propellant. In this thermite combustion, the flame consumes and spreads through discrete particles packed in a highly porous matrix. Because the physics of flame propagation in this arrangement entails flame spreading and is a strong function of the packing arrangement of particles and porous structure of the material, the term combustion wave speed will be used to characterize the velocity of the leading edge of the reaction zone.

Results

Ignition Sensitivity

Figure 3 is a sequence of still frame images illustrating ignition and flame propagation captured with the high-speed camera. Ignition occurs at the pellet center and propagates radially and axially along the pellet. The flame front is stable and planar and fully self-sustained.



Frame 3605
111.762 ms

Frame 3606
111.792 ms

Frame 3607
111.823 ms

Frame 3608
111.855 ms

Frame 3609
111.886 ms

Frame 3610
111.916 ms

Frame 3611
111.947 ms

Figure 3. Still frame images of ignition and flame propagation of a Al-MoO_3 pellet with a bimodal Al particle size distribution: 60% 80 nm and 40% 4 _m Al. The frame number and time from trigger are also given.

Figures 4 and 5 show the ignition delay time as a function of percent nano-Al within the mixture. The standard deviation bars represent the range of data measurements for between 4-6 pellets from each of the 11 mixtures, the data point corresponds to the average ignition delay time.

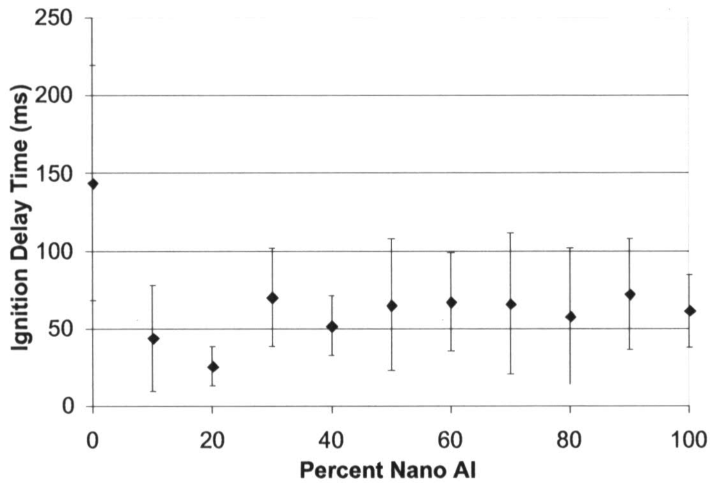


Figure 4. Ignition time as a function of percent 80 nm Al content for 4 _m Al

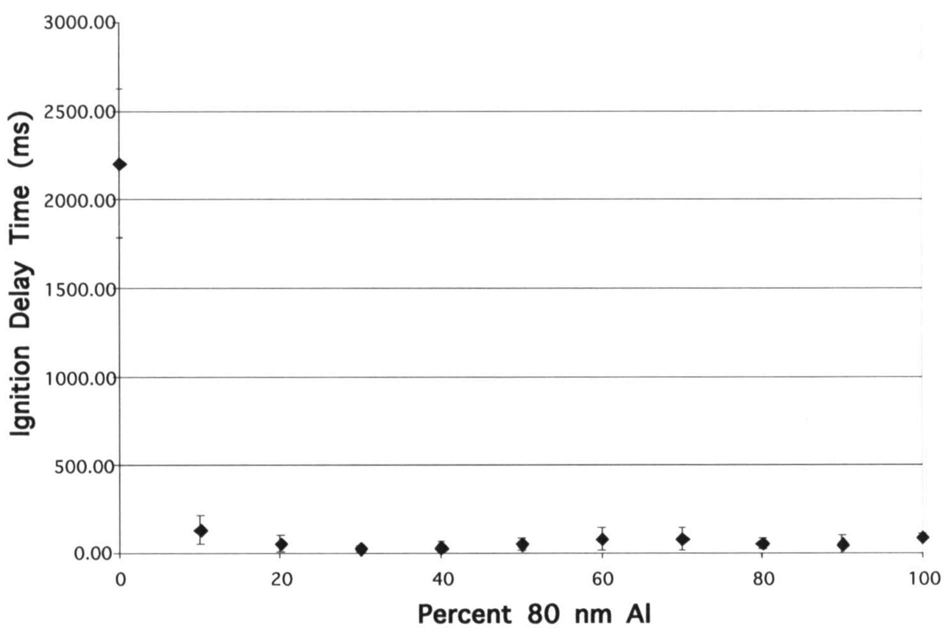


Figure 5. Ignition time as a function of percent 80 nm Al content for 20 _m Al

Wave Front Velocity

The combustion wave speed was measured using the Phantom IV diagnostic software and images recorded by the high speed camera. The following six frames shown in Figure 6 illustrate the nature of the self-propagating wave through a Al-MoO3 composite with an Al distribution of 60% 80 nm and 40% 4 _m.

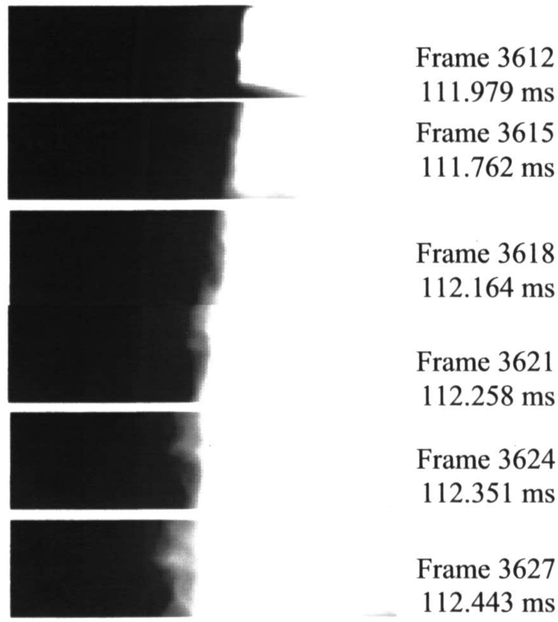


Figure 6 Pellet Combustion

The imaging software uses a designated light intensity transition and the elapsed time between frames to calculate the combustion wave speed. The combustion wave velocity for the 4 _m mixture is plotted as a function of 80 nm Al content in Figure 7. Also, Figure 8 shows the combustion wave speed of 20 _m Al plotted as a function of 80 nm Al content.

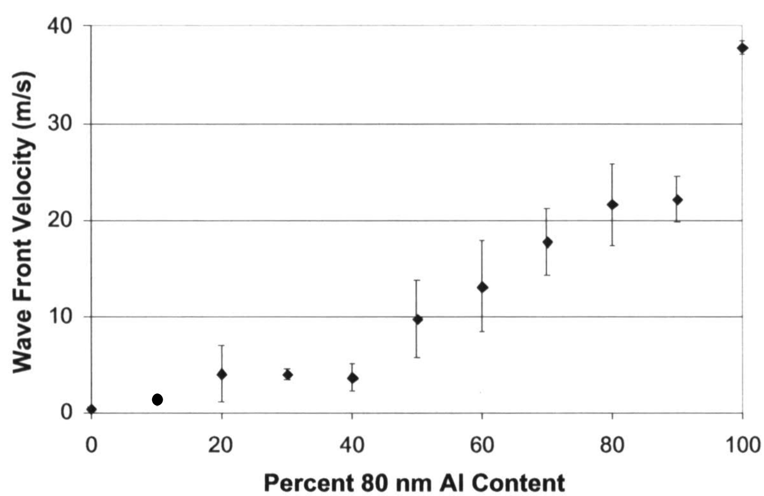


Figure 7. Combustion wave velocity vs. Percent 80 nm Al content for 4 _m Al.

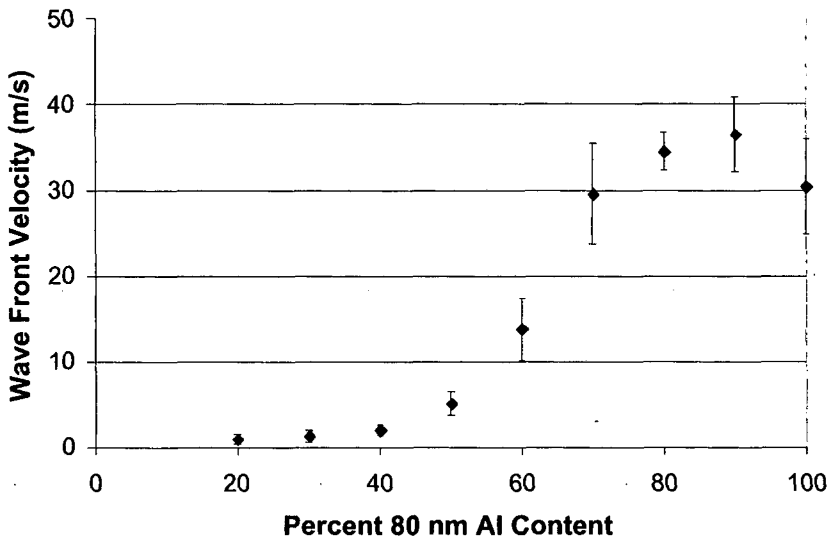


Figure 8. Combustion wave velocity vs. Percent 80 nm Al content for 20 _m Al.

In Figure 8, the data points for 0% and 10% 80 nm Al content are not shown. In the case of 0%, the pellet was exposed to the laser for a relatively long period of time before ignition of the pellet. The exposure to this heat flux volumetrically heated the pellet, compromising the ignition conditions. For this reason, the data point was not included. For the 10% 80 nm Al sample, the pellet could not sustain a self propagating wave.

Discussion

Ignition Sensitivity

Ignition of the pellet face begins in the center and burns radially to its round edge. Self-sustained flame propogation then occurs axially along the pellet in a planar manner.

The increased ignition sensitivity of mixtures with 80 nm Al begins with the unique melting properties of nano-sized metal particles. Previous studies have shown a melting point reduction of aluminum and tin due to decreases in particle size from the micron to nano range (ref.). Less energy is needed to melt the nano Al particles, which means the constant heat flux laser beam will melt these particles in less time than the melting of the micron Al particles. The melting of the nano-sized aluminum in the mixtures drives the ignition of the pellet.

Another contributing factor to the heightened ignition sensitivity is the large surface area to volume ratio that the 80 nm Al particles possess. This ratio for the 80 nm Al particle is over two orders of magnitude greater the ratio for the 20 um Al particles. This property is very important when the reaction begins. Also, the much smaller 80 nm Al particles can be in close proximity with many other particles of this size while filling voids between the 4 or 20 um Al particles. The Al_2O_3 passivation layer on the surface of the Al particles is amorphous, allowing fluid to penetrate this layer and come in contact with the active Al. During the first moments of ignition, 80 nm Al melts and comes in contact with the other nano Al particles in its close proximity. The amorphous oxide layer of the solid particles allows the molten Al to heat the aluminum to its melting point. The relatively large ratio of surface area to volume allows more heat per unit mass to be transferred, increasing the reactivity of the mixture.

Combustion Wave Speed

The combustion wave speeds shown in Figs. 7 and 8 increases from roughly 1 to 40 m/s as nanometer Al content increases. The most interesting behavior is observed in Fig. 8 in which a sharp transition from relatively slow to fast flame propagation occurs between 50 and 70 % nanometer Al content. A similar trend was previously observed in porous explosive charges and attributed to a transition from normal to convective burning [10]. When convective burning takes precedence over thermal conduction and radiation, energy and mass transfer in the burning zone are driven by gas jets that penetrate into the pores of the energetic material. Bobolev et al [10] showed that in some cases penetration of the combustion into the pores is followed by the establishment of a regime of stationary convective burning whose rate substantially exceeds the normal burning rate. In an effort to identify a this burning regime, an analysis of porous energetic material combustion under constant pressure conditions has lead to a stability criterion known as the Andreev number, An (Eq. (1)) [10]. This non-dimensional parameter is similar to the Peclet number except tailored for reacting flow through porous media.

$$\text{An}=\frac{\rho_b U d_h c_p}{k_g}=\text{const.} \tag{1}$$

In this equation, ρ_b is the bulk density of the composite, U is the measured combustion wave speed, d_h is the hydraulic pore diameter, c_p is the heat capacity of the composite and k_g is the thermal conductivity of the gas. If this value exceeds a certain constant, combustion penetrates into the porous structure and convective mechanisms dominate flame propagation.

In making this calculation it is necessary to estimate the hydraulic pore diameter, d_h, given from Eq. (2) [11].

$$d_h=\frac{4\varepsilon}{A_o(1-\varepsilon)} \tag{2}$$

In this equation ε is the void volume, A_o is the specific surface area based on the solid volume and is calculated as the solid surface area divided by the solid volume (A_s/V_s), and (1-ε) is the solid volume fraction. Table 2 shows the calculated values of each parameter for both the 4 and 20 micron containing bimodal mixtures. For each estimate, the An number is significantly less than 1.0. Bobolev et al [10] calculated critical An numbers between 3 and 10 and generalized that if the An $\geq$ 6.0 combustion will penetrate into the pores and convective mechanisms will play the primary role in accelerating the flame front.

The above analysis suggests that the transition from low to high combustion wave speeds may not result from a shift in the flame propagation mechanism. If conductive and radiative mechanisms remain dominant regardless of bimodal size distribution, then the nano-scale particles may exhibit unique thermal properties that enhance flame propagation.

Yang et al [8] showed nano-scale Al particles that can absorb more energy compared to their micron scale counterparts. The increased levels of absorbed energy may generate a more intense radiation field and elevate the temperature of the preheat zone, as depicted in Figure 9. Higher preheat temperatures will result increased combustion wave speeds. If too few nano-particles are present in the composite, the molten Al that expands out of the amorphous Al2O3 shell and oxidizes will not generate enough energy to heat coarser micron scale particles to their ignition temperature. The heat diffuses away from the localized reaction resulting in quenching of the reaction.

The effective thermal conductivity of the composite may also influence energy transport. The effective thermal conductivity is a function of the thermal conductivity values of each component within the matrix, the volume fraction, and the distribution of the matrix and dispersed phases(s). Hasselman and Donaldson [12] theoretically investigated the role of particle size in the effective thermal conductivity of composites and found that the presence of an interfacial thermal barrier could have a significant effect on composite thermal conductivity. In this system, the Al_2O_3 shell encapsulating nano-Al particles could represent an interfacial thermal barrier to some extent. As localized Al oxidation reactions occur, the highly amorphous Al2O3 may provide enough thermal insulation to facilitate localized energy build up. When energy is constrained, heat losses associated with thermal diffusion away from the localized reaction are reduced. As the number of Al nanoparticles increases within the matrix (Table 2), the surface area of the composite also increases. The matrix takes on the form of an aerogel. The effective thermal conducitivity is expected to vary in a sigmodial manner decreaseing as particle size decreases and surface area increases. Thus the heat released in the combstion of the nano-scale particles heats adjacent micron scale particles to their ignition temperature because of the low thermal conductivity of the mixture. Both the micron and nano-scale Al particles play a significant role in the reaction mechanism. The nanoparticles facilitate the initiation of the reaction and the micron particles help sustain high energy densities.

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