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Processing and characterization of aluminum-based nanothermites

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Abstract During the past several years, a significant effort has been on investigation of reaction front propagation and the rate of energy release in heterogeneous systems consisting of nanopowder reactants. Substantial size reduction of each reactant powder (e.g. from micro- to nano-size) leads to increase of reaction front propagation in some systems under unconfined conditions by approximately two to three order of magnitude. This paper presents key challenges associated with processing and use of nanothermite materials and characterization of nanoreactants. Reaction constants, such as activation energies and frequency factors were determined using DSC technique for several nanothermite systems based on nanosize aluminum and iron oxide, bismuth trioxide, and molybdenum trioxide. Experimental data of ignition delay times for different nanothermite systems using laser energy source were compared well to those predicted by proposed mathematical model.

Keywords Nanothermites · Mixing · Reaction kinetics · Combustion · Ignition

Introduction

In recent years researchers have found that energetic materials that are produced on the nanoscale have shown significantly improved performance, especially in the area of sensitivity, mechanical properties, and energy release. Metastable Intermolecular Composites (MICs) represent one example of such materials. These systems consist of metal nanopowder (e.g. aluminum) and oxidizers [1]. The MIC formulations are based on intimate mixing of reactants on the nanometer length scale [1–8]. As the specific surface area increases, the number of contact points between the reactants also increases and therefore the reaction rate increases [9]. Review of the recent literature on the combustion of pyrotechnic materials shows the relation between the reaction rate and an average particle size of reactants is significant [10–13]. The experimental studies have also shown that the reaction rate depends on other factors, including particle size distribution [13] and degree of intermixing [14]. Reaction rates between nanosize aluminum and metal oxides can be significantly greater than those observed with traditional micron-size thermite powders [1, 15, 16]. Reactions occurring between metal and metal oxide powders are accompanied by the generation of high temperatures (>3000 K) [17]. Super-thermites, formed by mixing aluminum and metal oxide nanopowders result in energy release rate by two orders of magnitude higher than similar mixtures consisting of micronsize reactants when reacted in a loose powdered form. These super-thermites may find an application in formulations of environmentally benign percussion primers, air bag initiators and inflators, as well as components of thermal batteries [18].

A typical combustion front propagation velocity in a condensed phase is of the order of several centimeters to a few meters per second. Conductive heat transfer and relatively large diffusion scales are two key rate-determining steps during the condensed-phase combustion. Examples of several thermite systems, together with corresponding heat of reaction, gas generation ability, and adiabatic temperature calculated at 1 atm. argon gas pressure are listed in Table 1 [19].

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Table 1 Thermodynamic properties of selected thermite reactions [19]

Thermite reaction	Q (cal/g)	Q (cal/cm^3)	Gas generation 1 atm (g gas/g mixture)	T_{ad} (K)
$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$	945.4	3947	0.0784	3135
$2Al + Bi_2O_3 \rightarrow 2Bi + Al_2O_3$	505.1	3638	0.894	3319[a]
$2Al + MoO_3 \rightarrow Mo + Al_2O_3$	1124	4279	0.2473	3688[a]
$2Al + WO_3 \rightarrow W + Al_2O_3$	696.4	3801	0.1463	3253
$2Al + 3CuO \rightarrow 3Cu + Al_2O_3$	974.1	4976	0.3431	2843

[a] Values calculated in this paper

During the past few years, a significant research effort has been made in the formation of reactive nanometer size powders (nanopowders), including reactive elements, such as aluminum [20, 21]. These powders are characterized by very high specific surface area (20–150 m^2/g). The average particle size of such powders is below 100 nm. Due to high surface area, these nanopowders might be pyrophoric when exposed to air or another oxidizing atmosphere. They can be handled in air environment only if a proper passivation layer is applied [20, 21].

This paper is focused on: (i) characterization of nanosize reactants used in nanothermite mixtures, (ii) protective coating of aluminum nanopowders, (iii) mixing of binary nanopowders, and (iv) investigation of ignition and combustion characteristics.

Experimental

Characterization of aluminum nanopowders

Different aluminum nanopowders (Novacentrix, IMP) were used in this experimental research. The average particle size of those nanoreactants varied from 40 to 120 nm. The content of reactive aluminum varied from 70 to 85 wt%. Copper, bismuth, molybdenum, and iron oxide nanopowders used in all experiments were obtained from the Nanophase Technologies Company, Accumet, Technanogy, and Alfa Aesar and had average particle sizes: 40, 160, 55, 10 nm, respectively. Silane material Z-6124, used in coating studies, was obtained from the Dow Corning Corporation.

A typical TEM photograph of passivated aluminum nanopowder is shown in Fig. 1. The oxide layer, approximately 2–3 nm is clearly visible in this image. X-ray analysis of that region indicates that this oxide layer is amorphous.

The most important parameters characterizing aluminum nanopowders are an average particle size and a content of reactive aluminum. In order to process aluminum nanopowders in air, a surface passivation layer is required. The most effective layer is formed by controlled oxidation of aluminum nanopowders. This layer protects aluminum from further oxidation by oxygen, however does not protect from the attack of moisture.

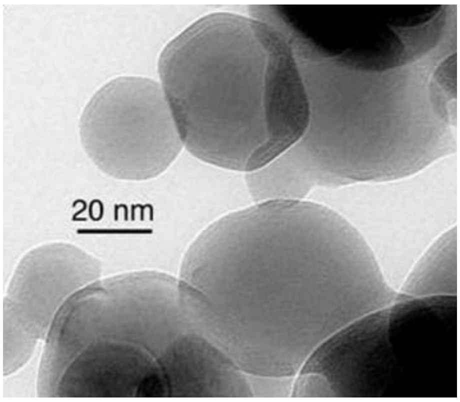


Fig. 1 TEM photograph of oxide passivated aluminum nanopowder

Recently, IMP developed a process of making aluminum nanoflakes by attrition milling of aluminum flakes. The same specific surface area and the reactive aluminum content can be obtained within few hours of milling but the morphology is drastically different from aluminum nanopowders formed by vapor condensation (spherical powder). SEM photograph of such milled powder is shown in Fig. 2.

Several techniques were tested to measure a reactive content of aluminum: (i) TG analysis, (ii) volumetric method; (iii) calorimetry; and (iv) LIBS. It was found that the volumetric method, which relies on a stoichiometric release of hydrogen during the reaction between aluminum and sodium hydroxide, seems to be very accurate and suitable, especially when aluminum powders coated with organic materials are analyzed. TG technique is reliable if aluminum is initially exposed to argon up to 400 °C in order to remove water, and later to oxygen. It is important to notice that the analyzed aluminum powder should be diluted with nanosize alumina (~10 wt%) in order to prevent melting of formed Al_2O_3, which may inhibit further oxidation of aluminum. Comparison of TGA and volumetric methods are presented in Table 2.

It was determined experimentally that any aluminum nanopowder is reacting with moisture when exposed to humid environments. Figure 3 shows the effect of humidity and time on the content of reactive aluminum in Al nanopowders with the average particle size of 50 nm.

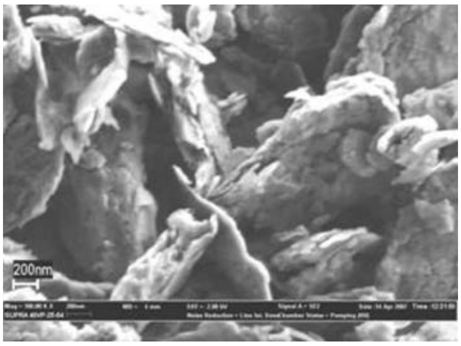


Fig. 2 SEM photograph of IMP aluminum nanoflakes

Table 2 Comparison of the amounts of reactive aluminum in nanopowders with different particle sizes determined by TG and volumetric methods [22]

Avg. particle size of aluminum nanopowder (nm)	TGA method (wt%)	Volumetric method (wt%)
50	67.9	68.0
80	75.1	79.8

It can be clearly seen that the content of reactive aluminum decreases very fast with time at higher humidity levels. Even at relatively low humidity levels (43%) the reaction progresses relatively fast. In order to reduce the effect of moisture, the same 50 nm aluminum nanopowder was coated with silanes or fatty acids. In both cases hydrophobic groups have had a significant effect on the reaction with moisture. Figure 4 shows the effect of silane Z-6124 from Dow Corning Corp. on the rate of reaction with moisture at 40 °C and 97% relative humidity. It was found that samples with the concentration of silane of 5 wt% are well protected over the extensive period of time.

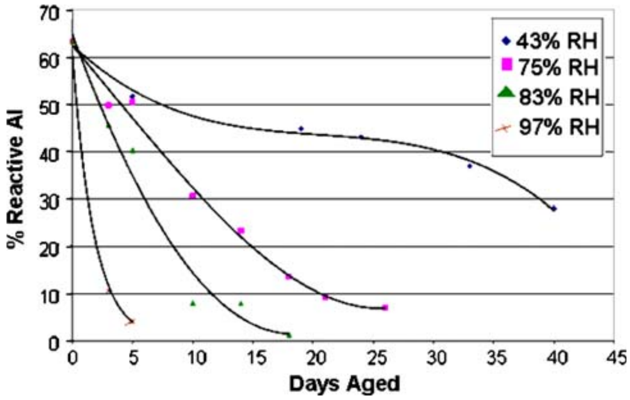


Fig. 3 The effect of relative humidity and time on the reactive aluminum content in oxide passivated Al nanopowders [22]

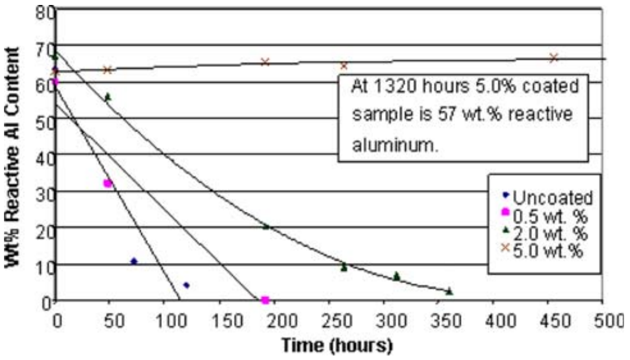


Fig. 4 The effect of silane Z-6124 coating and time on the content of aluminum in Al nanopowders at T = 40 °C and RH = 97% [22]

Mixing of binary nanopowders

One very important factor influencing the rate of energy release in MIC systems is the completeness of mixing process. It is well known that nanopowders can be mixed effectively in liquids only if they are well dispersed.

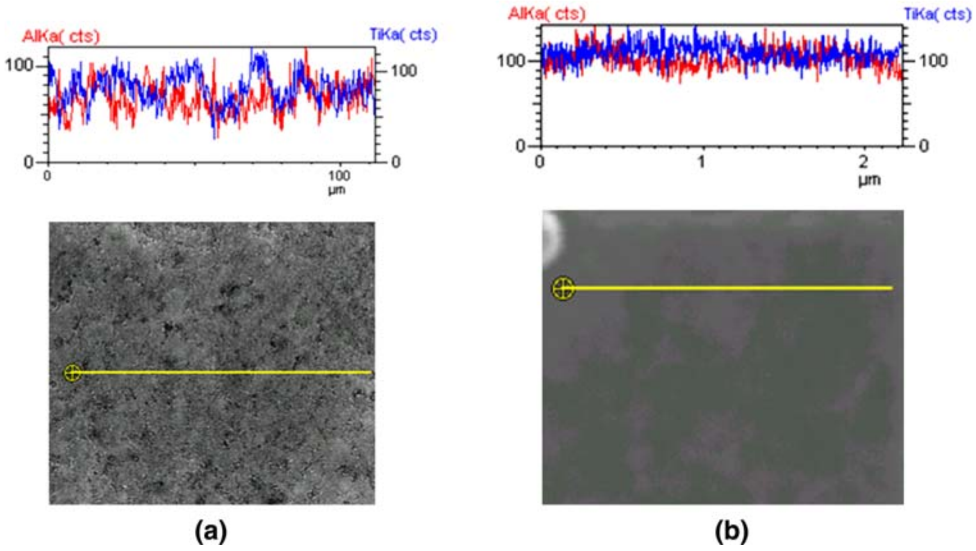
Silane coating leads to better dispersion of nanopowders and more uniform mixing in organic solvents. Use of other non-aqueous dispersants, such as sodium dioctyl sulfosuccinate, leads to similar mixing results. In order to evaluate the quality of mixing process SEM analyses of mixed samples were done. Figure 5 shows results from two mixing processes. In the first case (Fig. 5a) mixing of Al with average particle size of 50 nm and TiO_2 nanopowders with average particle size of 40 nm was done in hexane without any dispersants. In the second case, the same powders were mixed when 2 wt% sodium dioctyl sulfosuccinate was added into hexane. It can be clearly seen that the mixing in the presence of the dispersant is superior.

Recently, IMP developed water based mixing process. Mixtures consisting of Bi_2O_3 and Al nanopowders with the composition of 15 wt% of Al were successfully prepared without any significant reduction in the reactivity of nanothermites. Firstly, oxidizer powder was dispersed in water, followed by the addition of inhibitor solution in water. Finally, the mixing of aluminum and bismuth oxide nanopowders was conducted. The slurry's stabilizing agents and/or binders were added at the last stage of mixing. Dense slurry (density ~2.18 g/cm^3) was homogenized in an ultrasonic bath for 15 min before dispensing and drying. Excellent performance of percussion primers and other ignition devices was obtained from such slurry was obtained [23].

Reaction kinetics of binary nanothermites

Reaction kinetics and thermal ignition characteristics were investigated for Al–Bi_2O_3 by differential scanning

Fig. 5 Elemental line scan analyses of Ti and Al elements in Al–TiO_2 mixtures prepared by mixing in hexane **a** without dispersant, **b** with dispersant [22]



(a)

(b)

calorimetry. A procedure for determining activation energy and pre-exponential factor was developed and outlined by the American Society of Testing and Standards, Method E 698. This test method is designed for determining Arrhenius kinetic constants for thermally unstable materials. It requires a series of DSC experiments in which the sample under investigation is heated to the point of reaction at various heating rates from 1 to 20 K/min. For each heating rate, the peak reaction temperature is recorded. An approximate value for activation energy can be calculated using a plot of the log heat rate versus the inverse peak reaction temperature and the following equation:

$$E \cong -2.19R[d\log\beta/d(1/T)] \qquad (1)$$

where R is the gas constant, β is the heating rate in K/min, and T is the peak reaction temperature at the corresponding heating rate. Once the value of activation energy is calculated, the pre-exponential factor can be determined using the equation:

$$Z = \beta E e^{E/\mathrm{RT}} \Big/ \mathrm{RT} \qquad (2)$$

This procedure was used to compare kinetic constants, E and Z, for the Al–Bi_2O_3, Al–Fe_2O_3, and Al–MoO_3 systems. The effect of coating of aluminum nanopowder with oleic acid on activation energy in Al–Bi_2O_3 system was also determined.

It is known that a significant thermal energy barrier must be overcome in heterogeneous condensed phase exothermic reacting systems before ignition can occur. Earlier studies showed that thermal ignition of nanoenergetic mixtures occurs at temperatures below melting point of aluminum and below temperatures at which substantial sublimation or decomposition of corresponding oxides takes place [7, 24]. The limiting factor affecting the reaction prior to the ignition is diffusion in a solid phase. Therefore, the rate of diffusion can be correlated to the activation energy of the system. Using differential scanning calorimetry and the ASTM test method, it was confirmed that the activation energies for all three investigated nanothermite systems were indeed very high. Table 3 shows calculated activation energies, pre-exponential factors, and peak reaction temperatures at the heating rate of 10 °C/min.

Experimental data shows that the Al–MoO_3 system has the smallest thermal energy barrier and Al–Fe_2O_3 has the highest. The presence of a protective oleic acid coating on aluminum nanopowder in the Al–Bi_2O_3 system also shows an increase in the activation energy. The presence of oleic acid layer creates an addition diffusion barrier between both reactants.

The effect of bismuth oxide particle size on the peak reaction temperature was also investigated using the differential scanning calorimetry. Three different bismuth oxide powders were used, including Nanophase, Accumet, and coarse Clark powders [19]. Each oxide powder was

Table 3 Kinetic parameters for various nanoenergetic systems [19]

Reactive system	Activation energy (kJ/mole)	Pre-exponential factor (s^{-1})	Peak reaction temperature in °C at 10 °C/min
Al^a–Fe_2O_3	248	$1.9 \cdot 10^{13}$	565
Al^a–Bi_2O_3	222	$6.5 \cdot 10^{11}$	553
Al^a(coated)-Bi_2O_3	245	$1.4 \cdot 10^{13}$	562
Al^a–MoO_3	205	$1.0 \cdot 10^{11}$	547

[a] Aluminum nanopowder: Al-40-P with the average particle size of 50 nm added in the quantity corresponding to 20% of the required stoichiometric amount

mixed in the same ratio with Novacentrix Al-40-P aluminum powder. The results are shown in Fig. 6.

The ignition temperature increases with the increasing average particle size of bismuth trioxide reactant. This trend can be explained by lowering mass transfer rate caused by the reduction of effective contact area between the reactants.

Ignition and combustion front propagation characteristics of Al–Bi_2O_3 system

Open tray burn test method has been commonly used for characterization of the combustion front behavior and the measurement of a front velocity in nanoenergetic systems. Previously, it was found that the Al–Fe_2O_3 nanothermite system has a combustion front propagation velocity of approximately 30 m/s [25]. Combustion front propagation velocities in Al–CuO, Al–MoO_3, and Al–WO_3 nanothermites have shown over one order of magnitude higher values than Al–Fe_2O_3 system [25–27]. Experimental data for Al–Bi_2O_3 reacting systems obtained using the same setup showed combustion front velocity even higher than those previously reported. Figure 7 shows combustion front propagation velocity in Al–Bi_2O_3 system consisting of Al-80-P Nanotechnologies aluminum and nanosized Clark bismuth trioxide as a function of aluminum content in the mixture. When uncoated aluminum was used, the maximum combustion front propagation velocity was 617 m/s and the optimum ratio aluminum concentration 14.5 wt%. When aluminum nanopowder with 5 wt% oleic acid was used instead, the combustion front velocity increased to 757 m/s for the same fuel to oxide ratio.

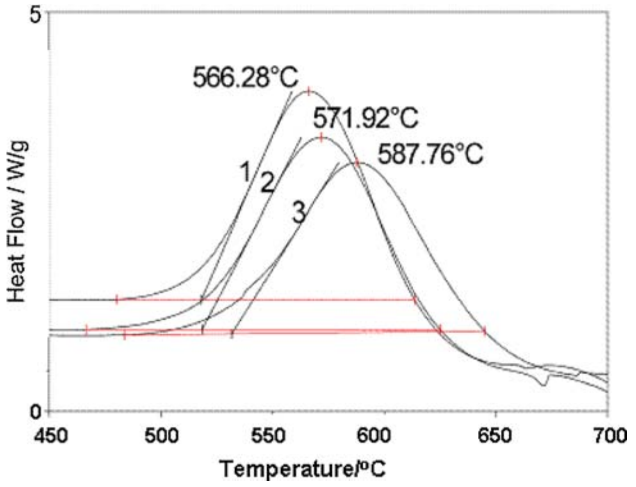


Fig. 6 DSC exothermic reaction peaks for Al–Bi_2O_3 nanothermite systems: (1) Nanophase Bi_2O_3; (2) Accumet Bi_2O_3; and (3) Clark Bi_2O_3

Under confined conditions, with a total volume of 0.2 mL, 30 mg of stoichiometric mixture of aluminum and bismuth nanopowders have generated pressure close to 70 bars (see Fig. 8).

In another experimental setup, described elsewhere [22], a reactive force was measured as a function of mass for the same three reacting systems. During these fast reactions, large localized pressure gradients are generated. Such localized pressure gradients create force on any surrounding stationary objects. Using a fast responding (µs response time) force load-cell, this effect was quantitatively measured. Experimental results showed that there was a linear dependence of force measured on mass of energetic mixture for each different system. The linear dependence was almost identical for the Al–CuO and Al–MoO_3 systems; however, the Al–Bi_2O_3 system had a greater slope and,

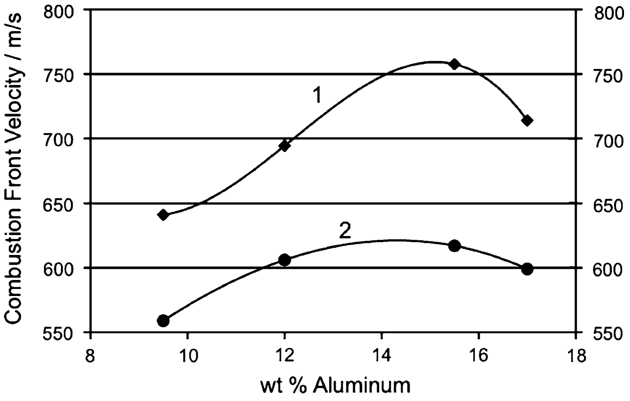


Fig. 7 Combustion front velocities in the Al–Bi_2O_3 system with coated (1) and uncoated (2) aluminum. The aluminum wt% was calculated as the ratio: mass of uncoated aluminum nanopowder per mass of uncoated aluminum and bismuth trioxide nanopowders [19]

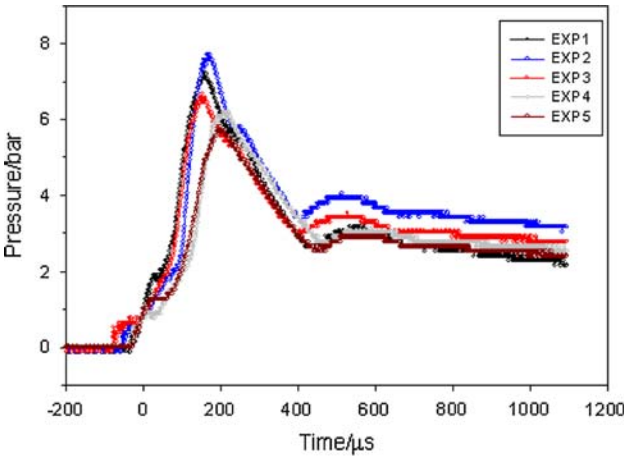


Fig. 8 Dynamic pressure responses of Al–Bi_2O_3 nanothermite system in the pressure cell having total volume of 0.2 mL

therefore produced a greater amount of force per unit mass. These results are shown in Fig. 9.

One method by which the thermal ignition sensitivity of a material can measured is through the use of a laser pulse. Using a laser of constant beam diameter and measurable power output, the thermal ignition sensitivity of a material can be determined by monitoring the time required for a self-sustaining reaction to begin at a certain energy output of the laser. Although the experimental procedure to determine thermal ignition sensitivity using a laser is fairly straightforward and the energy required is easily calculated from the power output of the laser and duration of pulse prior to ignition, there are many different factors that can affect the ignition delay time. These factors include material density, configuration of the material (i.e. powder, loosely pressed material, solid pellet), heat capacity, thermal conductivity, surface reflectivity, and kinetic parameters among others.

Laser ignition experiments were performed to investigate the effect of nanoenergetic material consolidation on ignition delay time and to compare results with those predicted by the mathematical model. In Fig. 10 experimental data of laser ignition of Al–Fe_2O_3 nanothermite system with different porosities using 1.7 W laser pulse are presented.

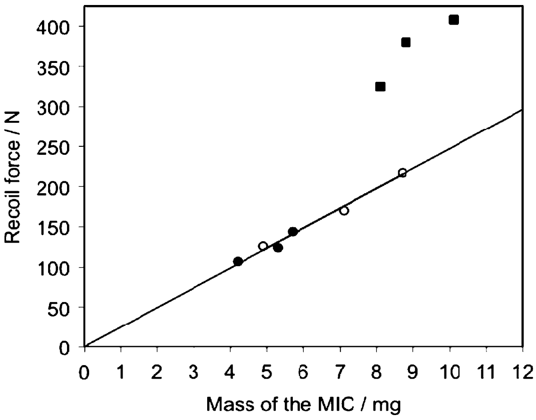


Fig. 9 Recoil force generated as a function of mass for nanoenergetic systems [22]

Mathematical modeling of ignition of nanothermites

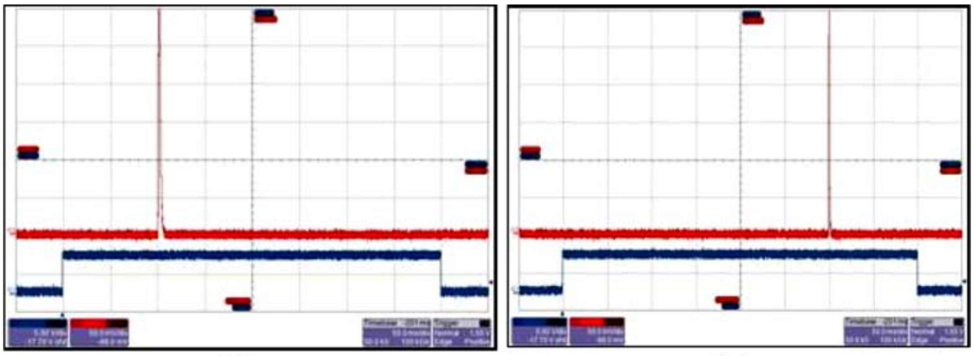
In order to determine the effect of such parameters on ignition delay time, as well as to investigate the dynamics of the system from the start of laser pulse to the point of ignition, we conducted mathematical modeling studies. In development of the mathematical model, we have made the following assumptions about the system being investigated [28, 29]:

- The system is 2-dimensional with cylindrical coordinates (z and r). There is no variation in the θ-direction.
- The system is a 2-component heterogeneous mixture but treated as isotropic.
- All physical properties are treated as constant for the duration of the run.
- No mass diffusion occurs.
- Heat conduction is modeling using Fourier's Law.
- The reaction rate constant is determined using the Arrhenius form to show temperature dependence.
- The proceeds as first-order with respect to the limiting reactant (fuel).
- The laser beam is considered to be a surface heat source only (no loss of material due to laser ablation occurs).

Using these assumptions, the governing energy equation for the system is as follows:

$$((1-\alpha)(\rho C_p)_s + \alpha(\rho C_p)_g)\frac{\partial T}{\partial t} = k\left[\frac{\partial^2 T}{\partial z^2} + \frac{1\partial}{r\partial r}\left(r\frac{\partial T}{\partial r}\right)\right] + q_{\text{reac}} \tag{1}$$

along with:



(a)

(b)

Fig. 10 Ignition delay measurements of the Al–Fe_2O_3 system as a loose powder (*left*) and in granulated form (*right*) using a 1.7 W laser pulse. Time scale for the plots is 0.05 s per grid mark

$$q_{\text{laser}} = q(r) = (1-\varphi)(2I_o/\pi r^2_{\text{beam}})e^{\left(\frac{-2r^2}{r^2_{\text{beam}}}\right)} \quad (2)$$

$$q_{\text{reac}} = k_o C_o (1-\eta) e^{(-E_a/\text{RT})} (-\Delta H)_r \quad (3)$$

and:

$$\frac{\partial \eta}{\partial t} = k_o C_o (1-\eta) e^{(-E_a/\text{RT})} \quad (4)$$

where ρ = density; C_p = heat capacity; T = temperature; t = time; k = thermal conductivity; z = axial coordinate; r = radial coordinate; q = heat input or heat loss; ϕ = reflectivity; I_o = laser power; r_{beam} = laser beam radius; k_o = pre-exponential factor; C_o = initial fuel concentration; E_a = activation energy; R = gas constant; σ = Stefan-Boltzmann constant; ε = emissivity; η = conversion; ΔH_r = heat of reaction; α = porosity; subscripts: s = solids; g = gas.

The following initial and boundary conditions are considered to exist:

$$t = 0: \quad 0 \le z \le Z_f \quad \text{and} \quad 0 \le r \le R: \quad T = T_o \quad (5)$$

$$t > 0: \quad r = 0: \quad \frac{\partial T}{\partial r} = 0 \quad (6)$$

$$r = R: \quad \frac{\partial T}{\partial r} = 0 \quad (7)$$

$$z = Z_f: \quad \frac{\partial T}{\partial z} = 0 \quad (8)$$

$$z = 0: \quad -k\frac{\partial T}{\partial z} = q_{\text{laser}}(r) - h(T - T_o) - \sigma\varepsilon(T^4 - T_o^4) \quad (9)$$

Using the equations and boundary conditions listed, explicit finite element analysis was performed over the entire mesh of points defining the system being investigated. This allows for one or several parameters to be varied in order to determine their significance in affecting ignition delay time.

Utilizing this model, the Al–Fe_2O_3 system was investigated to determine the effect of porosity and thermal conductivity on the ignition delay time of nanoenergetic mixtures and also as a comparison to experimental results for ignition delay time obtained for that system. Tests were run at values of 0.7 and 0.9 for porosity, constant laser power of 1.7 W, and thermal conductivity values of 2.0 and 0.4 W/m-K for the 0.7 and 0.9 porosity values, respectively. The kinetic data were used as presented above.

It was expected that the system with a porosity of 0.7 would have a significantly longer ignition delay time due to a higher total sample heat capacity and its thermal conductivity, allowing for the energetic material to dissipate the absorbed heat better throughout the sample. Ignition of the material was assumed to be at the point of thermal runaway in the system. Figure 11 shows the temperature profile versus time at the center of the top surface of material, directly where the most energy is absorbed from the laser beam. It can be seen from the plot that the laser gradually heats the material during approximately 0.22 s, at which point, ignition, and subsequently thermal runaway reaction occurs. This point of thermal runaway corresponds to a limiting reactant conversion value of 0.07. The temperature profile of the entire system being modeled at the point of ignition is shown in Fig. 12. It is shown in that figure that the temperature distribution is very concentrated at near the surface of the material that is heated by a laser pulse. Although the heat is dissipated throughout the sample, at the

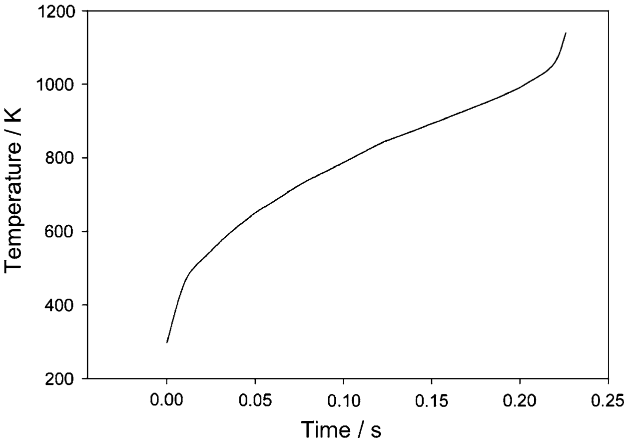


Fig. 11 Temperature versus time profile for top surface of Al–Fe_2O_3 system with porosity of 0.9 and laser power of 1.7 W

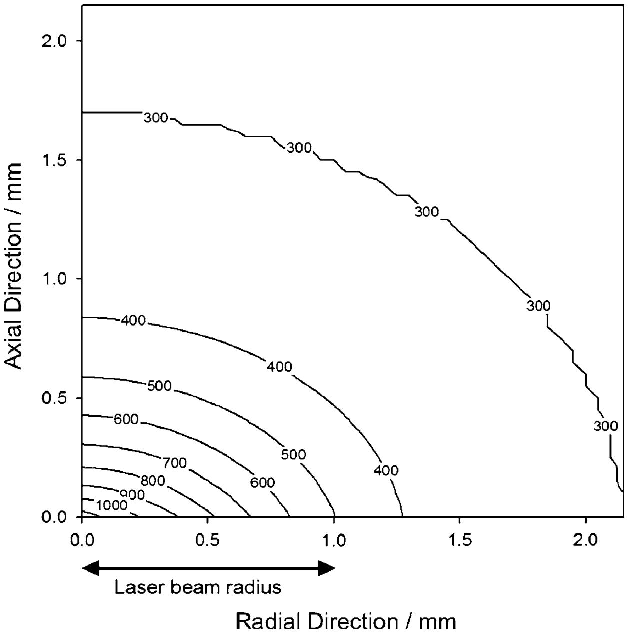


Fig. 12 Temperature (K) contours in Al–Fe_2O_3 system at point of ignition (t = 0.22 s)

Table 4 Comparison of experimental data to predicted results from mathematical modeling for laser-pulse ignition of nanothermites [29]

Nanothermite system	Ignition delay time (ms) modeling	Ignition delay time (ms) experimental
Al–Fe_2O_3 powder	1.53	2.24
Al–MoO_3 powder	1.26	1.52
Al–Bi_2O_3 powder	1.24	1.3
Al–Bi_2O_3 granule	13	11

point of ignition, the majority of the sample is insignificantly heated, indicating that in order for ignition to occur; only a hot spot is needed as opposed to having the entire sample reaching its ignition point. Results, from the test run with a porosity of 0.7, show a significant increase in ignition delay time of over 2 s, indicating that heat capacity and thermal conductivity are very important factors and can be affected by the degree of consolidation.

Four different systems were investigated using both laser ignition experiments and mathematical modeling. These include Al–Bi_2O_3, Al–MoO_3, and Al–Fe_2O_3 powders with a porosity of ~90% and granular Al–Bi_2O_3 with a porosity of ~70%. Results from both the experiments and mathematical model are shown in Table 4.

Conclusions

- It was shown that wet mixing in the presence of dispersants is very important to obtain mixtures with high concentration uniformity.
- Protective organic coatings with hydrophobic groups are essential to protect aluminum nanopowder from the reaction with moisture at higher relative humidity levels.
- Ignition delay time is not affected by the quantity of the ignited mixture but is a strong function of the reactant concentration and the amount of organic coating.
- Effective method of mixing aluminum nanopowder with bismuth trioxide and or iron oxide powders in water was developed.
- ESD sensitivity of nanothermites is affected by particle size and morphology, degree of consolidation and rate at which energy is deposited into the sample.
- Laser ignition time depends on thermal and kinetic properties of the nanothermite material as well as porosity and rate of energy input.

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