Investigation of Reaction Mechanisms and Combustion Characteristics of Nanothermites

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Abstract

Nanoenergetic mixtures, although sometimes classified as thermite composites, do not react in the same manner as conventional thermite mixtures. Due to the smaller particle size and higher surface area, the rate of energy release is several orders of magnitude higher. This research study has been focused on the investigation of mechanisms of energy release in nanoscale thermite mixtures such as Al-Fe_2O_3 and Al-CuO. High speed video was used to monitor the reaction front propagation of these nanoenergetic mixtures inside small diameter tubes. This series of tests was intended to characterize the transition from slow to fast reaction rates as well as monitor the effects of pressure and confinement on reaction front propagation. Differential scanning calorimetry and closed volume pressure cell tests were performed to determine the effect of gaseous atmosphere on both reaction rate and energy output of the nano-thermite mixtures.

Introduction

Since the emergence of energetic mixtures comprised of nanoscale powders, research efforts have grown in an attempt to characterize these materials and find uses in practical applications. While nanothermite mixtures have been incorporated in such applications as lead-free electric matches [1] and lead-free percussion primers, much of the research towards characterization has focused on unconfined burning of the material with little emphasis on determining the mechanisms and kinetics of reaction.

This research study focused on investigation of the combustion front propagation under unconfined, semi-confined and confined configurations in order to better understand the mechanisms by which the reaction is driven. Experiments were also carried out in a confined volume cell to determine the effect of gaseous atmosphere on reaction rate and reactive power of several different systems including Al-CuO, Al-MoO_3, and Al-Bi_2O_3. Differential scanning calorimetry was also used to determine kinetic parameters that can be used in modeling studies. These parameters were activation energy and frequency factor.

Experimental

Combustion Front Propagation in Small Diameter Tubes

Small diameter tubes were used to provide confinement for the nanothermite mixtures during reaction while still allowing for the combustion front to be monitored using high speed video. The system investigated in these studies was Al-Fe_2O_3. The mixture consisted of 38.4 wt% Nanotechnologies 50nm Al and 61.6 wt% Nanophase Fe_2O_3. Approximately 100mg of the mixture was placed inside a small diameter acrylic tube with dimensions of 1/8 inches inside diameter and 1.5 inches long. The tube was then encased in an acrylic block for safety confinement. This setup allowed for both ends of the tube to be left open during reaction or for one or both end of the tube to be blocked during reaction to control the direction in which the pressure is release. Two different experiments were recorded at 4000 fps with a high speed video camera. In the first experiment, both ends of the tube were left open to the atmosphere so pressure could be released in two directions. The nanothermite mixture was ignited at one end of the tube by flame. In the second experiment, the end of the tube opposite ignition was sealed so pressure could only be released in one direction. In this case, the mixture was ignited at the end opposite to the sealed end.

Confined-Volume Pressure Cell Tests

One of the methods used for determining reactive power of the nanothermite systems and the effect of gaseous atmosphere on that reactive power is by measuring the pressure output during reaction in a closed volume cell. A small amount (20-30 mg) of the nanothermite mixture was weighed out and placed in a sample cup. The cup is lowered and sealed inside the closed-volume cell. The mixture is spark ignited via piezoelectric igniter. A piezoelectric pressure transducer sends a voltage signal to and oscilloscope which records the signal and can then be converted to pressure. Experiments were performed with various initial pressures of both air and argon atmospheres.

Determination of Kinetic Parameters for Nanothermite Systems

Another step towards characterizing these nanoenergetics systems is the development of a rate law that defines the reaction kinetics of the system. An important kinetic constant that can be experimentally determined is activation energy. The method used to do this is the ASTM Standard method. This technique involved the use of differential scanning calorimetry (DSC) to determine the peak reaction temperature over a range of different heating rates. The heat rate for the sample is varied over the range of 1 to 20 K/min until at least 3 data points are collected for peak reaction temperature. Once the data points are collected, the log of the heat rate, β, in K/min is plotted against 1/T, where T is the peak reaction temperature in Kelvin. An approximate value for the activation energy can then be calculated using the following formula:

$$\mathbf{E = -2.19R[d\ \log_{10} \beta/d(1/T)]}$$

If the data plot as a straight line, the value for $[d\ \log_{10} \beta/d(1/T)]$ is the slope of the line. The second kinetic parameter calculated from the experimental results is the frequency factor. The frequency factor, also known as the pre-exponential factor, can be calculated using the formula:

$$\mathbf{Z = \beta E e^{E/RT}/RT^2}$$

where β is the heating rate from the middle of the range.

Two different systems were investigated using this method. The first system was Al-Fe_2O_3 with a 10 wt% fuel ratio. The dilute system was used to prevent rapid reaction that might damage the equipment. An SDT Q600 Simultaneous TGA/DSC was used in the analysis. Samples of the system were heated to 900 ^oC at heat rates of 5, 10 and 15 K/min. The second system investigated was $Al\text{-}Bi_2O_3$. The same ratio of fuel to oxide was used as in the $Al\text{-}Fe_2O_3$ tests. Samples were again heated to 900 ^oC at rates of 5, 10 and 20 K/min.

Results

Propagation Mechanisms in Small Diameter Tubes

The first experiment performed using the small diameter tube setup allowed for both ends of the tube to remain open to the atmosphere. In this case, any pressure generated during the reaction, either by vaporization of reactants and products or by expansion of gas due to heating, would be released in two directions. Since pressure is relieved in the path of least resistance, the initial pressure release would be in the direction of ignition as the unreacted powder would provide hindrance to the flow of gases. As the reaction proceeds, however, the gradient of pressure drop in the direction of the combustion front propagation will increase to the point where the unreacted powder will not provide enough hindrance to the pressure release and the reaction will accelerate. Figure 1 shows still frames of the combustion front during the reaction at equal time intervals of 0.0125s starting at t = 0.

Figure 1 shows that as the reaction proceeds and the gradient of pressure drop in the direction of propagation increases, the combustion front accelerates. This corresponds with the theory that the driving mechanism behind the reaction is convection. As the hot gases are forced forward into the unreacted material, the reaction accelerates and eventually reaches a point where the pressure drop is great enough to expel unreacted powder from the end of the tube where it then ignites as a cloud of suspended particles.

The second experiment performed using the tube setup involved blocking the end of the tube opposite ignition to prevent and pressure from being released in the direction of the combustion front propagation. This setup would prevent hot gases from being forced forward into the unreacted material and in theory, prevent acceleration of the reaction front. Figure 2 shows video stills of the combustion front as it propagates through the tube.

As the reaction starts, the pressure in the tube quickly builds up to the pressure generated by the reaction front, thereby eliminating any significant pressure drop in the direction of the combustion front propagation. With no pressure gradient, the reaction cannot accelerate and reaches steady state almost immediately as shown in Figure 2.

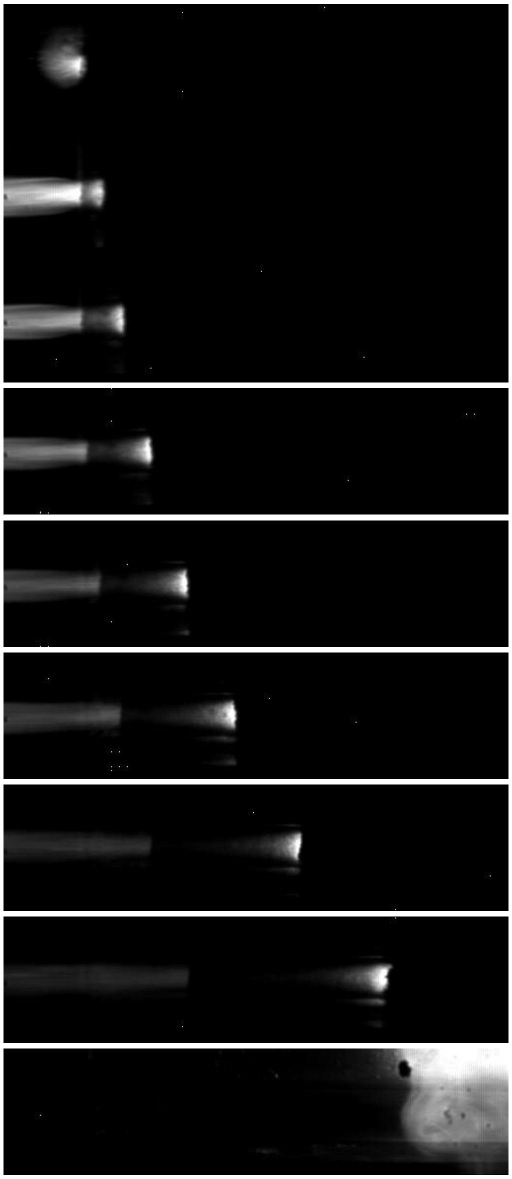

Figure 1. High-speed Video Stills of Propagation With Both Tube Ends Left Open (0.0125 s increments).

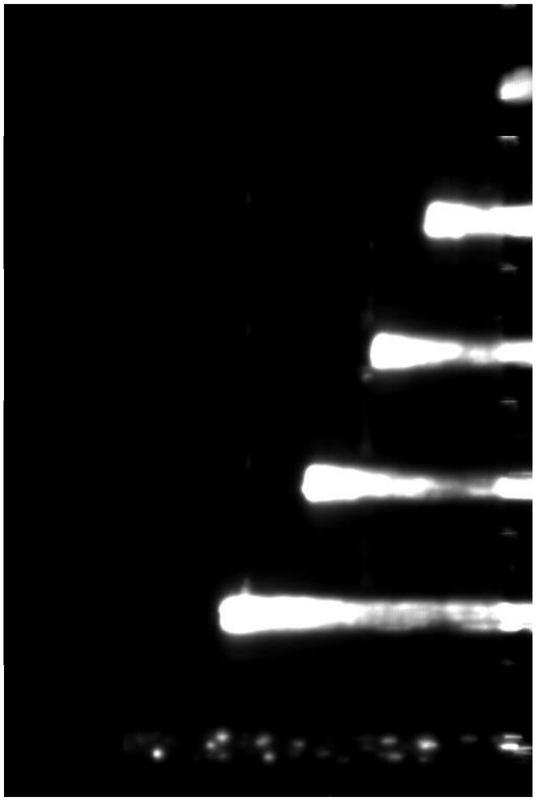

Figure 2. High-speed Video Stills of Propagation With the Tube End Opposite Ignition Blocked (0.02 s increments).

Effect of Gaseous Atmosphere on Energy Output

For the comparison of reactive power between the different systems, a vacuum was pulled on the reaction cell after the sample was lowered in and sealed to remove all atmospheric air. They cell was then purged with argon to a pressure of 0 psig to assure that any reaction is between the two components and not with the gaseous atmosphere present in the cell. The mixture was then ignited via piezoelectric spark and the peak voltage from the oscilloscope was converted to peak pressure for each system. The pressure spikes for the three systems are shown in Figure 3. The system with the greatest reactive power was Al-Bi_2O_3 with 92 psig, followed by Al-MoO_3 with 67 psig and Al-CuO with 52 psig. This ranking of systems according to reactive power also corresponds with combustion front propagation velocity measurements for the three systems.

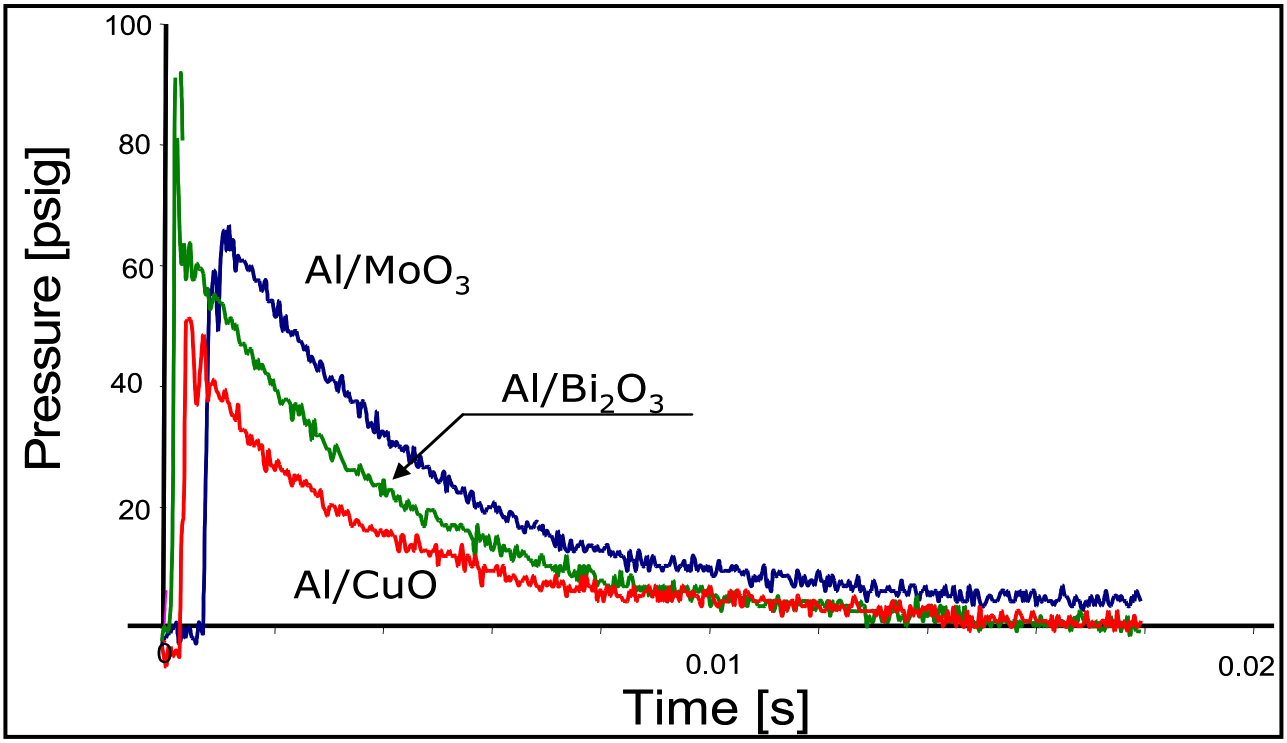

Figure 3. Pressure Response For Various Reactive Systems Under 0 PSIG Argon. [2]

Since all of the tests performed were done in 0 psig initial atmosphere, it was desired to measure the effect of initial gas pressure on peak pressure of the reaction. The Al-CuO system was used for these tests and peak pressure was measured for reacting systems with 0, 15 and 30 psig initial pressure of Argon. In order of increasing initial pressure, the peak pressures were 62 psig, 82 psig and 99 psig. This series of tests showed that in argon, the increase in the initial pressure did not have a significant effect on the peak pressure other than an increase by approximately the same amount as the increase in the initial pressure over the previous run.

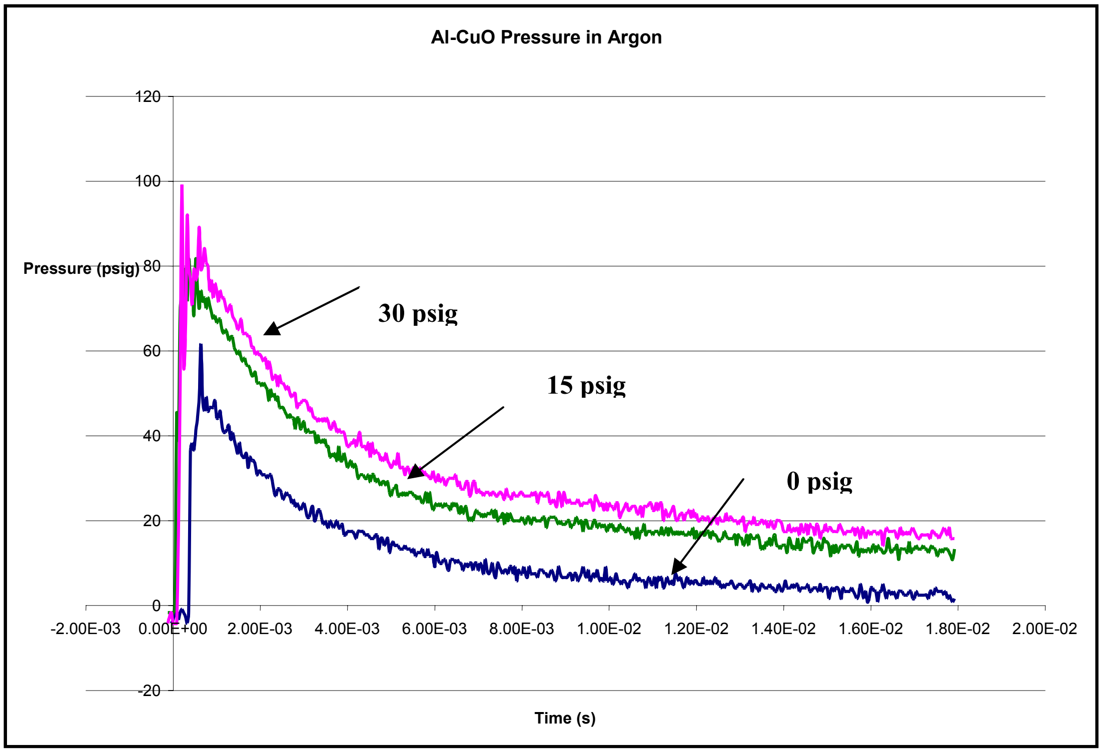

Figure 4. Pressure Plot of Al-CuO with Varying Initial Pressures of Argon.

Since argon is an inert gas, a second set of tests were done with air as the initial gas. Aluminum is known to react with both oxygen and nitrogen from the atmosphere so it was hypothesized that an increase in the initial pressure of air would have a greater effect than an increase in the initial pressure of argon. Using the Al-CuO systems again, three tests were run at 0, 15 and 30 psig initial pressure of air. Figure 5 shows that the initial increase from 0 to 15 psig has a significant effect on the increase in peak pressure. The results for peak pressure during the 15 and 30 psig initial tests were also higher than the corresponding initial pressures of argon.

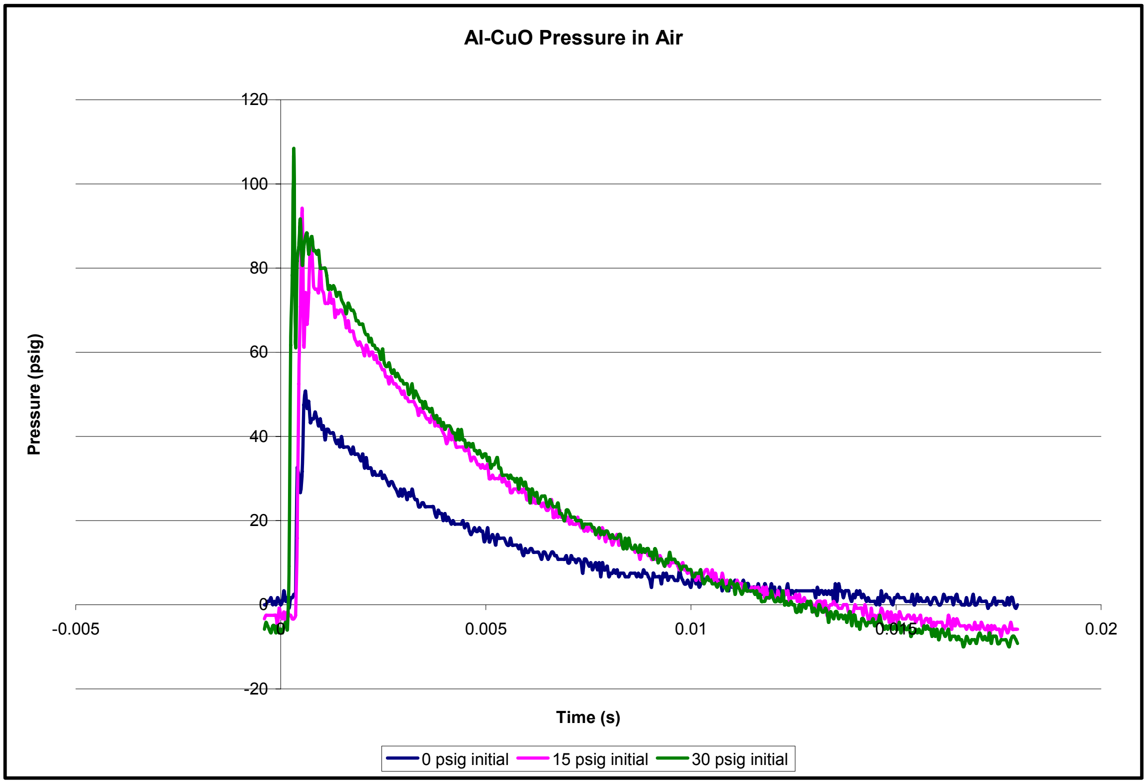

Figure 5. Pressure Plot of Al-CuO with Varying Initial Pressures of Air [2].

Kinetic Parameters of Activation Energy and Frequency Factor

Using the procedure described above, tests on the Al-Fe_2O_3 systems showed peak reaction temperatures of 551, 566 and 577 ^{o}C respectively. When the data were plotted using the method described above, the plot was linear and calculations determined an activation energy of 247.76 kJ/mol for the system. The frequency factor was calculated to be $1.147*10^{15}$ min^{-1}. The second system investigated was Al-Bi_2O_3. The same ratio of fuel to oxide was used as in the Al-Fe_2O_3 tests. Samples were again heated to 900 ^{o}C at rates of 5, 10 and 20 K/min, resulting in temperature peaks of 536, 553 and 571 ^{o}C. The plot of the data again resulted in a straight line. Using the value of the slope, the activation energy for the system was calculated to be 221.5 kJ/mol and the frequency factor was $3.872*10^{13}$ min^{-1}.

Conclusions

Results from the experimental research presented in this paper has allowed for several conclusions to be made about the nature of nanothermite mixtures and their reactive properties and capabilities. These conclusions are:

- The gradient of pressure drop during the reaction of nanothermite mixtures in small diameter tubes has a significant effect on the propagation of the combustion front. As the pressure drop in the direction of the propagation becomes greater, the reaction front accelerates. When there is little or no significant pressure drop gradient, the reaction reaches steady state.

- Determination of kinetic parameters for the Al-Fe2O3 and Al-Bi2O3 systems using differential scanning calorimetry gave values for activation energy and frequency factor of 247.76 kJ/mol and $1.147*10^{15}$ min^{-1} for Al-Fe_2O_3 and 221.5 kJ/mol and $3.872*10^{13}$ min^{-1} for Al-Bi_2O_3.
- Closed volume pressure cell tests indicated that the most powerful system in terms of pressure output when reacted in argon was the Al-Bi_2O_3 system, followed by Al-MoO_3 and Al-CuO.
- When testing the Al-CuO system in varying initial pressures of air and argon, it was determined that an increase in initial pressure resulted in an increase in pressure output of the system during reaction. The experiments also showed that the Al-CuO system performed better in air than argon.

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