Tunability of Nanoenergetic Materials

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Abstract

Expansive research in the area of nanoenergetics over the past several years has led to the discovery and development of a wide array of reactive systems. These reactive systems have many varying properties including: ignition sensitivity, reaction rate, adiabatic reaction temperature, pressure generation, and theoretic maximum density. Additional investigations into the factors affecting ignition and reaction characteristics have shown that many physical and chemical properties of the individual reactants, as well as processing methods, can have a significant effect on the overall behavior of the nanoenergetic system. Application of nanoenergetic materials as components of various products requires that the ignition and reaction characteristics be tailored to have specific sensitivities and energy outputs. This research effort addressed how ignition sensitivity thresholds, reaction rate, and pressure generation can be tailored to have a wide range of values. Several different individual reactants are used including: aluminum nanopowder, iron oxide nanopowders, bismuth oxide nanopowders, and additional binders and gasifying agents. The primary system of interest in this research consisted of aluminum with both iron oxide and bismuth oxide incorporated as oxidizing agents. The effect of stepwise increases in iron oxide content on pressure generation is shown, as well as the effect of consolidation on ESD sensitivity. The use of nitrocellulose as a gasifying agent is also presented along with its effect on pressurization rate, peak pressure generation, and ESD sensitivity.

Introduction

There are many different methods by which the ignition and reaction parameters of nanothermite systems can be modified. This paper will focus on certain methods that can be used to modify or 'tune' specific properties including: electrostatic discharge (ESD) sensitivity, ignition delay time, pressure generation, and pressurization rate. ESD sensitivity for nanothermite systems can range from the microjoule level, as exhibited by loose powder Al-Bi_2O_3, to tens of millijoules for consolidated systems[1]. Ignition delay is dependent on the rate at which energy is added to the sample and the form of the energy (i.e. laser, electrostatic discharge, flame) in addition to the physical and chemical properties of the individual nanothermite system[2]. Pressures generated during reaction of the nanothermite are due to two different processes; expansion due to heating of surrounding gases and evolution of gaseous products. The latter of these processes generally produces much higher pressures. Pressurization rate is obviously proportional to the reaction rate as pressures generated by both processes subside after a period of time due to cooling and condensation of gaseous products.

With the wide variety of nanoscale fuels and oxidizers available on the commercial market today, different nanothermite mixtures can be made to provide near limitless combinations of the reaction properties listed above. Individual properties of materials that can affect reaction rates include: particle size, specific surface area, particle morphology, and the physical-chemical nature of the material[3]. It stands to reason that if specific reaction properties for an application are required, one or more of these material properties could be changed to achieve the desired result. This process of developing a mixture with specific properties by changing the material being used, however, is a very tedious process that has several potential complications. These complications include the fact that there are no direct correlations to be made between nanothermite systems containing different types of fuels or oxidizers, and that suppliers do not necessarily produce the exact same quality of product from batch to batch. In a fast growing field like nanotechnology, suppliers of nanoscale reactions also come and go quickly. Because of this, it is not always possible to procure a reactant with the exact same physical properties over a long period of time.

Tuning of nanothermite materials, on the other hand, is a process by which the reaction parameters are controlled by varying concentrations of reactants, methods of mixing, degree of consolidation of the material, use of binders, and incorporation of gas generating agents. These methods are less reliant on having specific reactant properties such as particle size and specific surface area because most of them can be changed on a stepwise level to adjust the reaction parameters. This makes it easier to fit a specific nanoenergetic material to a specific application with less guess and check work as is necessary when using different types and sizes of reactants to do so. The research presented in this paper is mainly focused on nanothermite systems based on nanoscale aluminum as a fuel. Previous studies have investigated different loose powder nanothermite systems including Al-Fe_2O_3, Al-CuO, Al-MoO_3, Al-WO_3, and Al-Bi_2O_3[4-7]. These studies have shown the Al-Fe_2O_3 and Al-Bi_2O_3 systems to have significantly different reaction properties. The system containing iron oxide reacts much slower and produces much lower pressures where as the system containing bismuth oxide has a very fast reaction rate and produces a significant amount of gaseous products. Based on these results, it was hypothesized that including both iron oxide and bismuth oxide in the reactive mixture in various ratios could make a nanothermite material with reaction properties covering the entire spectrum between the two systems. Other methods for tuning reaction parameters to be discussed include method of processing, use and amount of binder to form consolidated material, and coating of material in gasifying agents to increase pressure and decrease sensitivity.

Experimental

Two different methods of mixing nanothermite reactants were used in this research, each resulting in the formation of a different form of nanothermite material. The first method, used to make loose powder nanothermite, involves combining the reactants in isopropyl alcohol and mixing the components ultrasonically in the absence of binders. Upon thorough mixing, the slurry was then poured into a grounded metal drying pan to evaporate the solvent and yield the loose powder material. The second method involves processing the reactants in water with the inclusion of a binder material. This method eliminated the use of flammable solvents but came with a drawback. If untreated, aluminum nanopowders will react with water for form aluminum oxide. To counteract this, 2.5 wt% of ammonium dihydrogen phosphate, with respect to the mass of aluminum nanopowders, was added to the water prior to adding aluminum. A water soluble binder material, such as arabic gum or methyl cellulose, was dissolved into the solution as well at 4-6 wt% with respect to the total nanothermite reactant mass. The metal oxide was then finally added and the thick slurry was ultrasonically mixed. Upon mixing, the slurry was then micro-pipetted into a grounded metal drying tray to form small granular material.

Pressure output of the material was measured using one of two closed volume pressure cells shown in Figure 1. The first pressure cell has an internal volume of 20 cc. The nanothermite material is ignited by a laser-pulse directed through a glass window and the pressure is measured using a piezoelectric pressure transducer from PCB Piezotronics. The second pressure cell has a much smaller internal volume of 2.75 cc to measure higher pressures produce under more confined conditions. This setup using a Ni-Cr wire coil to ignite the nanothermite material. Again, a piezoelectric pressure transducer is used to measure dynamic pressure.

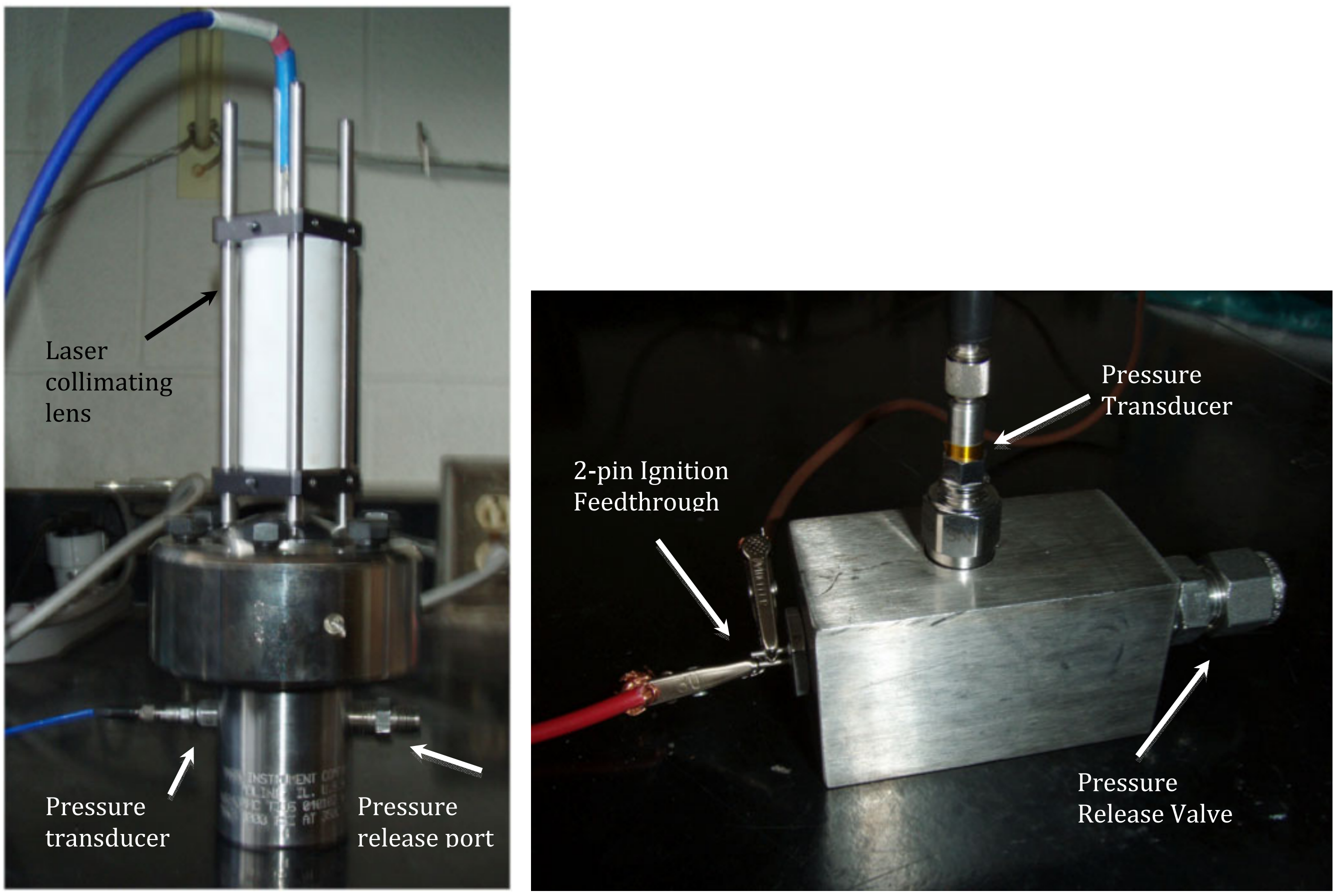

Figure 1: Closed volume-pressure cell for measuring dynamic pressure response of nanothermite reaction. Internal volume of (20cc left, 2.75 cc right).

Another important reaction property, aside from pressure generation, is sensitivity of the material to ignition, especially by electrostatic discharge (ESD). ESD testing of the materials was performed using a Model 930D-FTS Electrostatic Discharge Simulator from Electro-Tech Systems, Inc. The apparatus allowed for the easy exchange of capacitance over the range of 100 pF to 20 nF. The voltage level could also be varied over the range of 0 – 5000 V. In accordance with standard military testing of materials for ESD sensitivity, each sample was subjected to 20 consecutive discharges as a specific energy level. If no ignition occurred, the voltage and/or capacitance were increased and the sample was again subjected to 20 consecutive discharges at the new energy level until ignition occurred. The lowest energy level at which ignition occurred is the ignition threshold.

Results

In order for future development of products containing nanothermite materials, we have focused on systems based on a combination of aluminum nanopowders fuel with various ratios of iron oxide and bismuth oxide nanopowders. Fe_2O_3 and Bi_2O_3 each have different reaction properties when combined with aluminum. Iron oxide reacts relatively slowly (tens of m/s) with aluminum compared to bismuth oxide (hundreds of m/s) and also generates much less gas upon combustion (~8% by weight vs. ~89% by weight for bismuth oxide)[8]. Certain applications require fast combustion rates and high pressures while others require controlled reaction rates with hot particulate reaction products. In order to investigate the effect of iron oxide content on reactivity, the mass % with respect to total oxide was increased incrementally and pressure evolution during reaction was recorded. For each test, ~35 mg of nanothermite mixture was ignited by laser impulse in a closed volume pressure cell with an internal volume of 20 cc. Figure 2 shows the effect of increasing iron oxide content on the peak pressure generated during reaction.

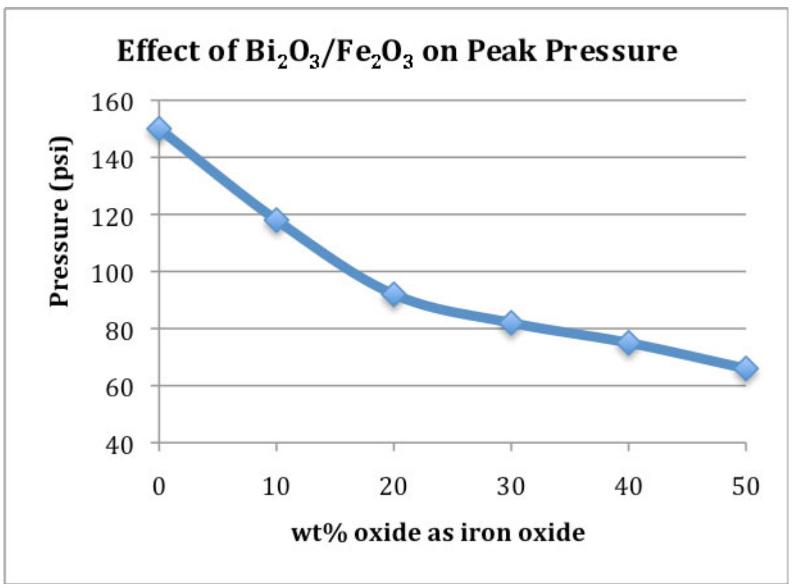

Figure 2: Plot of peak pressure generated as a function of iron oxide mass percentage of total oxide content.

In order to investigate the effect of consolidation, it was determined that a mixture of aluminum nanopowder combined with a 50/50 molar ratio of iron oxide and bismuth oxide would produce significant pressure upon reaction while also yielding molten iron particulates. The inclusion of iron oxide also slows the reaction down enough to allow for longer interaction time with subsequent propellants that may need to be ignited by the nanothermite. Nanoenergetics containing iron oxide are also less sensitive to ignition than those containing only bismuth oxide as the oxidizer. Water-based processing was used to render the resultant energetic material into granular form. A thick slurry containing 18.7 wt% of 80 nm aluminum from Novacentrix, 20.8 wt% of 30 nm iron oxide from Nanophase Materials, and 60.5 wt% of 416 nm bismuth oxide from Accumet Materials, along with 4 wt% arabic gum binder was micropipetted into grounded metal drying trays.

In order to measure the ESD sensitivity of the material in consolidated form, several granules were placed in close proximity to each other and the discharge tip of the ESD gun was lowered into the group of granules. Using this procedure, the minimum energy at which 20 consecutive discharges could not be completed without at least one ignition was 1.6 mJ, a value much higher than the loose powder ignition threshold

Replacing conventional materials in various applications usually requires that certain reaction parameters are either matched or exceeded. The two important factors that needed to be investigated were pressurization rate and peak pressure generated. Burning of propellants requires the containment of the gases produced to drive the reaction faster and produce high pressures. Proper testing of these materials required the construction of a smaller 2.75 cc volume pressure cell. Pressure generation for the combustion of nanothermite granules is shown in Figure 3.

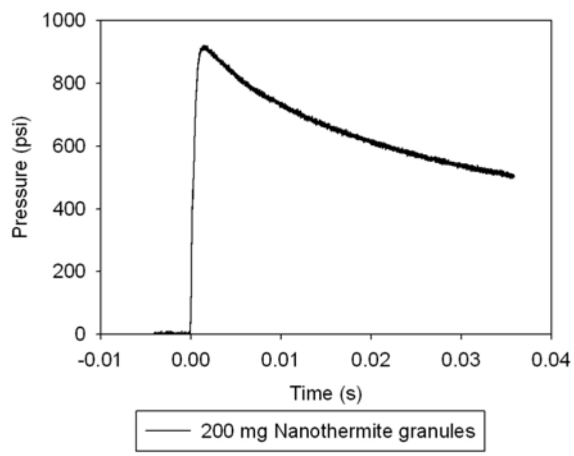

Figure 3: Pressure generation of nanothermite granules

Since it can be seen that the nanothermite reaches its peak pressure quickly and then begins to sharply drop off, it was decided to coat the granular material in a gasifying agent to slow down reaction and produce higher pressures. The first agent considered was nitrocellulose, due to the fact that its byproducts are not environmentally harmful and it is a common component in pyrotechnic materials. One drawback of trying to incorporate nitrocellulose into the granules is that it water insoluble and the granules are formed using a water-based process. To get around this obstacle, it was decided to add the nitrocellulose in the form of a coating on the outside of the granules once they have been formed and dried. A solution of nitrocellulose dissolved in acetone was made. This solution could then be spray onto the dried granules. Since the binder material used in the granules is water soluble, there was minimal penetration of nitrocellulose or acetone into the pores of the granules. Once the acetone is evaporated from the granules, the nitrocellulose remained as a coating on the outer surface. Not only did the coating slow down pressurization rate and increase peak pressure as is shown in Figure 4, but the ESD sensitivity was mitigated to the point that 25 mJ was not sufficient to ignite the granules.

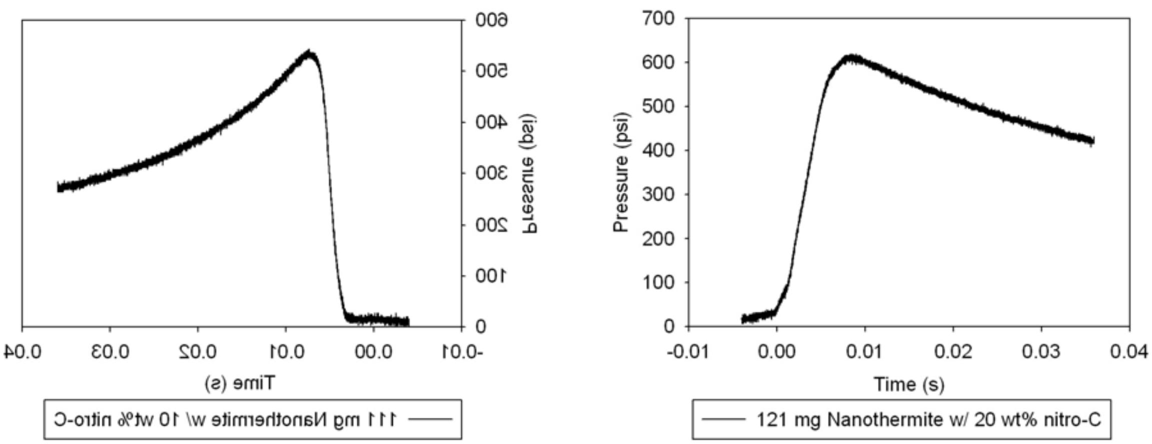

Figure 4: Pressure plots of nanothermite granules coated with 10 wt% nitrocellulose (left) and 20 wt% nitrocellulose (right).

Conclusions

It has been shown that the reactivity and ignition sensitivity of nanothermite systems can be tuned to a specific level using several different techniques. The incorporation of both iron oxide and bismuth oxide, at various ratios with respect to each other, into a nanothermite mixture containing aluminum is an easy and effect way to develop a material with specific reaction rate, pressure output, and ignition sensitivity. Other effective methods for changing reaction parameters of a material include consolidation of the material into granular form and coating of the granular material with gasifying agents.

References

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