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Abstract

Composite energetic materials combine fuel and oxidizers for high energy density exothermic reactions and are used for ordnance, industrial and localized power generation applications. This study focuses on examining an additive to a mixture of aluminum (Al) and copper oxide (CuO) to decrease ignition sensitivity under accidental fire exposure conditions. Ammonium nitrate (AN) was incorporated into Al+CuO, as a 1:1 replacement for CuO, for varied equivalence ratios and examined for ignition and combustion when exposed to slow and fast heating rate ignition conditions. The goal was to develop an Al+CuO+AN formulation that would perform comparable to Al+CuO when intentionally ignited, but would not ignite in an accidental fire. Experimental results show that Al+CuO+AN with an equivalence ratio (ER) ranging from 4.0-5.5 inerts the reactants when exposed to slow heating conditions, yet ignites with comparative combustion performance to the baseline Al+CuO mixture when exposed to fast heating conditions. These results are consistent with thermochemical simulations of the heat of combustion and adiabatic flame temperature for the respective reactions. This study presents a new approach for tailoring composite energetic materials toward accidental fire safety by exploiting the early stage decomposition kinetics of AN, which are activated only by slow heating ignition conditions.

Key Words Thermites; Safety; Aluminum; Ammonium Nitrate; Ignition Sensitivity; Combustion; Energetic Materials

1.0 Introduction

Composite energetic materials (CEM) are mixtures of discretely separated fuel and oxidizer materials that combine to produce highly exothermic reactions. For example, the heat of combustion of aluminum (Al) fuel particles combined with copper oxide (CuO) particles is 21 kJ/cm^3 [1], which is significantly greater than that of a monomolecular explosive such as trinitrotoluene (TNT), which has a heat of combustion of 8 kJ/cm^3 [2]. While CEM offer high energy density, their reaction is diffusion limited such that they fall short of matching the power produced by explosives [3]. Yet, CEM can be tailored toward an application. For example, high gas generating mixtures have potential for use in micro-thrusters [4], high flame temperature mixtures are ideal for welding and alloying metals [5], and many aluminum-based mixtures are used as primers in ordnance systems, replacing harmful lead-based formulations [6]. With wide-spread integration of these materials in industry, their potential for unintentional ignition becomes an increased safety concern.

Accidental explosions in pyrotechnic plants [7-9], for example, have prompted research on ways to desensitize composites to electrostatic discharge (ESD) ignition. Small concentrations of carbon black, and more recently, carbon nanotubes (CNT) have been shown to channel current through a composite without igniting the energetic [10 -12]. The CNT offer a conduit for ESD energy, bypassing the reactants in the composite. For micron scale powders, as little as 4 volume % CNT will desensitize a mixture to ESD ignition [13].

In a similar vein, protection from unintended ignition in an accidental fire is also an important safety consideration. Accidental fires typically produce slower heating rate conditions

than igniters. Hydrocarbon based fires can produce heating rates on the order of 100 degrees per minute [14]. In contrast, igniters in ordnance systems produce heating rates on the order of 10^6degrees per minute [15, 16].

This variation in heating rate enables the design and synthesis of CEM that only enable ignition when heated at a specific (high) heating rate. If the CEM is heated at lower heating rates, an additive to the CEM would decompose prior to the auto-ignition temperature and render the CEM inert. The ideal additive allows the mixture to respond to specific ignition stimuli with optimum combustion performance while preventing ignition when exposed to other stray or unintentional stimuli. This is a new direction for exploiting the tuneability of composite energetic materials and important for the full life-cycle safe handling of these materials.

To accomplish this goal, we started with a well characterized energetic composite for its increased safety to ESD stimuli [17]. The mixture is composed of micron scale aluminum (Al) particles combined with copper oxide (CuO) particles and mixed to a specified stoichiometry. To this base mixture, carbon nanotubes (CNT) were added to obtain 4 vol % concentration. This mixture has been shown to be desensitized to ESD ignition and also shown that the CNT additive has negligible effect on the mixtures overall combustion behavior [13]. For these reasons, starting with a base mixture insensitive to ESD ignition and tuning it toward insensitivity to fire exposure would advance the development of an overall safer formulation. The objective of this research was to introduce another additive that would make this formulation inert when subjected to slow heating processes (i.e., an accidental fire). To accomplish this neutralization, portions of the CuO were replaced with ammonium nitrate (AN) additive. Many additives were considered, but AN was selected based on its relatively low decomposition temperature (i.e., 210°C [18]). The decomposition kinetics of AN have been well studied [19-21]. Generally, as

long as chloride and some transition metal ions (e.g., chromium and copper) are not included in the reactants (because they can catalyze AN decomposition), then the heat liberated upon decomposition is 36 kJ/mole [18, 22]. This is well below the apparent activation energy for many aluminum based energetics (i.e., 162 kJ/mol) [23]. In this way, AN could feasibly replace enough CuO such that under slow heating conditions AN decomposition would render the entire mixture too fuel rich to ignite. If AN decomposition can be activated for slow heating rate conditions, this mechanism could affect the accidental fire safety for a plethora of energetic composites.

2.0 Material and Methods

2.1 Material Preparation

The multi-walled carbon nanotubes (CNT) have an outer diameter of 20 nm, an inner diameter of 3 nm, and a length varying from 0.1-10 microns. Aluminum (Al) powder has an average spherical particle diameter of 4.0 microns and copper oxide ((CuO) powder has an average spherical particle diameter of 50 nm. All powders were procured from Alpha Aesar (Ward Hill, MA). The AN was procured from Sigma Aldrich (St. Louis, MO) with average prill size of 1 mm.

The mixture was designed to examine various stoichiometric proportions of CuO and AN oxidizer combination with Al as shown in the following reaction, Eq. (1). For every mole of CuO removed, 1.00 mole of AN is added (i.e., a 1:1 ratio of CuO:AN was used). It is also noted

that 4 vol% CNT is added to all mixtures but not assumed as an active participant in the reaction. The CNT additive was included to desensitize the mixture to ESD ignition.

$$3CuO + 3NH_4NO_3 + 4Al \rightarrow 2Al_2O_3 + 3Cu + 3N_2 + 6H_2O \qquad \text{Eq. (1)}$$

Stoichiometry is defined in terms of equivalence ratio (ER) and is the ratio of fuel/oxidizer mass ratio in the actual mixture to the fuel/oxidizer mass ratio in a stoichiometric mixture (see Eq. (1)). In this way, mixtures with ER > 1.0 are fuel rich (e.g. for stoichiometric ER = 1.0).

Once proportioned, the reactants were suspended in hexanes and sonicated in a Misonix S3000 sonicator for a total of one minute in ten second intervals. Sonication has been shown to be effective for producing homogeneous composites [10]. Post sonication, the mixtures were poured into a Pyrex® dish and the hexane evaporated while in a fume hood. The mixed powder was then reclaimed for further experimentation.

Mixtures were prepared for ER ranging from 1.0 - 5.5. For each ER, two mixtures were prepared: (1) Al+CuO+CNT (i.e., baseline mixture); and (2) Al+CuO+CNT+AN (i.e., AN additive mixture) such that the AN additive replacing a portion of CuO could be compared to the baseline mixture without AN.

2.2 Experimental Methods

Three stages of experimentation included: evaluating combustion pre-heat treatment, exposing samples to heat treatment simulating accidental fire, and evaluating combustion post-heat treatment. In all stages experiments were performed in triplicate to establish repeatability.

In the first stage, a 50 mg powder sample for each ER was ignited with a hot wire and the combustion was recorded using a high speed camera (see **Fig. 1** for schematic of setup). A Nichrome wire is a common hot wire ignition source and provides in excess of 10^6 degrees per

minute heating rate stimulus [24]. A variable voltage source was used to apply 15 volts to the Nichrome wire in order to achieve the temperature required for ignition. A Phantom v7 (Vision Research) high speed camera was used to record the combustion event using an F-Stop of 25 and captured images at 10,000 frames per second.

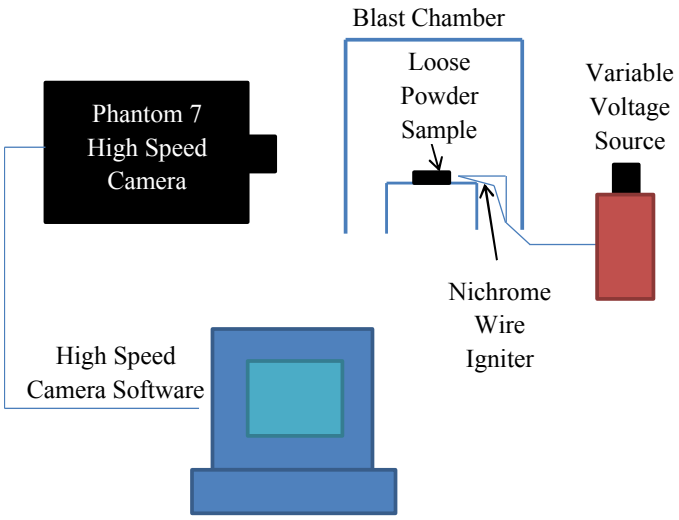


Figure 1. Experimental setup including high speed camera, blast chamber housing sample and Nichrome wire ignition system.

The second stage of experimentation exposed each 50 mg sample to simulated accidental fire conditions using a vacuum oven (NeyTech Qex) in an air environment. The samples were heated at 10 degrees per minute from room temperature to 230°C and held at this temperature for 1 hour, then cooled to room temperature. An InstruNet (model 100) data acquisition board and InstruNet software were used to record temperature. This pre-heat temperature is purposefully above the decomposition temperature of AN so that the effects of AN decomposition on combustion could be evaluated. While varying the heating rate to simulate a variety of fire

exposure conditions was considered, these initial tests were performed for one heating rate to establish the feasibility of this approach.

In the third stage, post-heat treatment, 50 mg samples were ignited using Nichrome wire and combustion recorded with the high speed camera at the same operating conditions prior to heat treatment and shown in **Fig. 1**. Post-heat treatment, the optimum sample stoichiometries did not ignite to the point that they could maintain self-sustained energy propagation.

As a further evaluation of these optimum stoichiometries, pre- and post-heat treated samples were examined for their ability to ignite another energetic mixture using a flame tube apparatus. In this setup, the tube is 10 cm long with 5 mm inside diameter (see **Fig. 2**). This apparatus is commonly used to quantify one-dimensional energy propagation in terms of flame speed for powder CEM [24, 25]. For this test, half of the tube was filled with 125 mg of pre- or post-heat treated sample and the other half was filled with 125 mg of an ignition sensitive mixture of nano-scale particles of aluminum and molybdenum trioxide ($Al + MoO_3$) [26]. This is one of the most ignition sensitive mixtures and a conservative evaluation of the pre- and post-heat treated sample ability to initiate a secondary reaction.

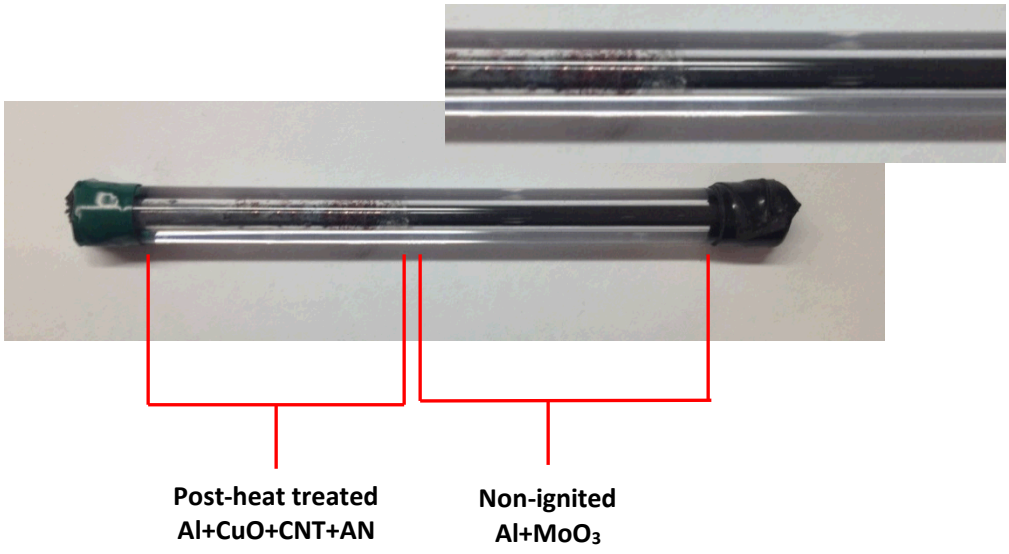


Figure 2. Flame tube apparatus shown AFTER an experiment in which the post-heat treated primer formulation with an ER = 4.0 was ignited but did not ignite the highly ignition sensitive Al+MoO_3 powder thermite. An enlarged view of the tube at the junction of the two powders is shown as an inset.

3.0 Results and Discussion

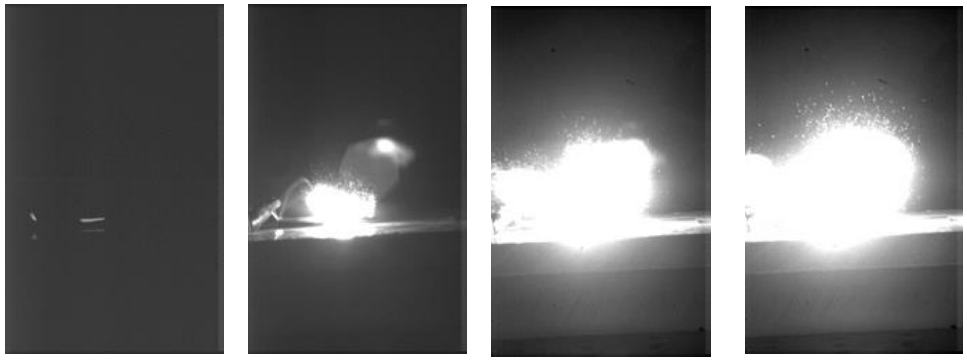
Table 1 summarizes the results. The most interesting finding is that an ER = 4.0 is a threshold for activation of the decomposition mechanism that was designed to inert the entire mixture post-heat treatment. This is the ER for which unsustained propagation and a non-ignition was repeatedly observed.

Table 1. Results of response to Al+CuO+CNT+AN formulations pre- and post-heat treatment as a function of equivalence ratio (ER). Notes provide more perspective on observations.

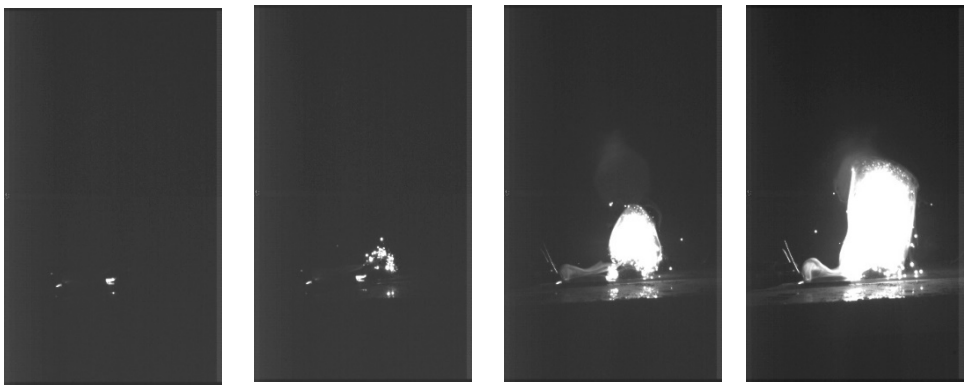
ER	Pre-Heat Treatment Ignition	Post-Heat Treatment Ignition	Notes
1.6	YES	N/A	Ignited during bake
1.7	YES	YES	
1.8	YES	YES	
2.2	YES	YES	
2.3	YES	YES	
2.3(AN Only)	YES	NO	Complete AN decomposition preventing post-heat treatment ignition
3.0	YES	YES	
3.5	YES	NO/YES	Non-repeatable results
4.0	YES	NO	Small amount of propagation but not self-sustained
4.5	YES	NO	Almost no propagation
5.0	YES	NO	No propagation but entire 50mg sample was red hot and turned to ash
5.5	YES	NO	Similar to 5.0 but powder pile exhibited slower heating

6.0	YES	NO	Similar to 5.5 but even slower. No visible flame.

All of the samples that included AN demonstrated comparable visual combustion to the baseline Al+CuO+CNT at the corresponding equivalence ratio pre-heat treatment. AN effectively replaced CuO in 1:1 molar ratios and maintained comparable combustion behavior. **Figure 3** shows still frame images of ER = 4.0 threshold case. Notice that the baseline mixture (see **Fig. 3A**) and the AN additive mixture (**Fig. 3B**) demonstrate similar reactivity prior to heat treatment. However, post-heat treatment (**Fig. 3C**), the mixture does not achieve a self-sustained reaction.



A



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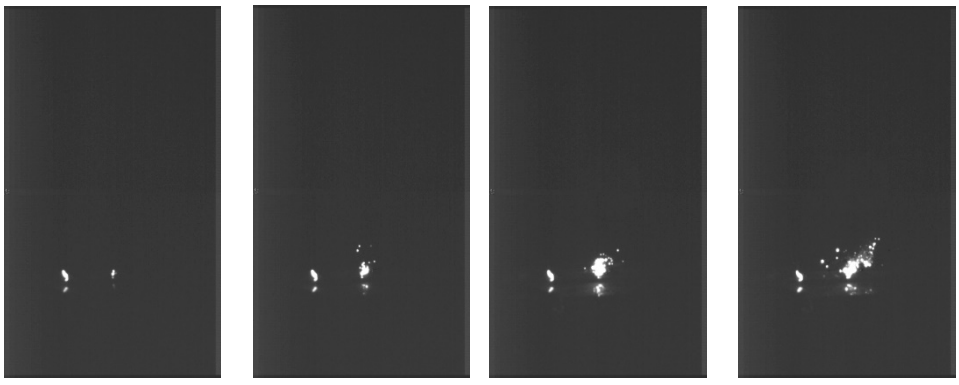
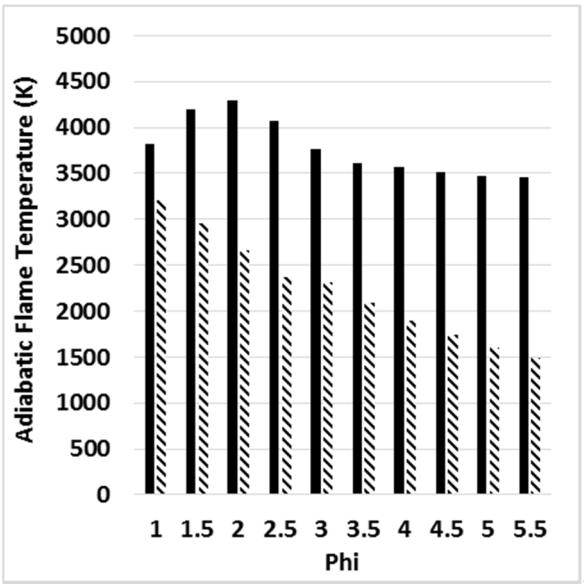


C

Figure 3. Representative still frame images of A. Al+CuO+CNT reaction; B. Al+CuO+CNT+AN reaction pre-heat treatment; and, C. Al+CuO+CNT+AN reaction post-heat treatment, all at ER = 4.0

Thermal chemical calculations for the above reactions were performed using REAL code simulation software (Timtec L.L.C.) for constant specific volume of 0.001 m^3/kg and an internal energy equal to zero. Both adiabatic flame temperature (**Fig. 4A**) and heat of combustion (**Fig. 4B**) as a function of equivalence ratio ranging from 1.0-5.5 were simulated. In the post-heat treated simulations the assumption is that AN does not participate in the reaction such that the products H_2O and N_2 do not exist. The simulations indicate that post-heat treatment decomposition of AN renders the reaction excessively fuel rich such that flame temperatures drop below the limit for a self-sustaining propagation, identified as 2000K [27, 28]. In fact, for 4.0 ER, the flame temperature drops just below the 2000K limit corresponding well with our experimental observations of limited reactivity for that formulation (see **Fig. 3C**). AT ER = 3.5 results are unrepeatable (Table 1), possibly because the 2000 K threshold for energy propagation is just barely achieved theoretically. Pre-heat treatment flame temperatures and heats of combustion are comparable for all formulations examined, such that these simulations are also an indication that AN does not significantly reduce the reactivity of the baseline mixture.

A 

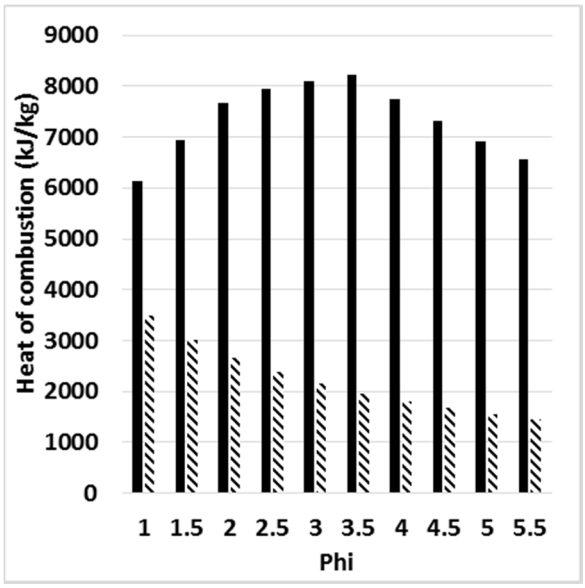
.B. 

Figure 4. REAL code simulations for the reaction in Eq. (1) with varying stoichiometry from 1.0 to 5.5 equivalence ratio (i.e., Phi). Solid bars represent pre-heat treatment and hatched bars represent post-heat treatment. Post-heat treatment simulations (i.e., hatched bars) assume no AN in reactants and no H_2O or N_2 in products. A. adiabatic flame temperature; and, B. heat of combustion.

Optimum stoichiometries (i.e., ER = 4.0 and 4.5) that passed the pre-heat treatment test and showed non-ignition post-heat treatment, were further tested as primer candidates using the flame tube apparatus described in **Fig. 2**. Pre-heat treatment Al+CuO+CNT+AN successfully ignited the Al+MoO_3 mixture. Post-heat treatment, the Al+MoO_3 could not ignite. This assessment was performed for multiple tests to establish repeatability.

4.0 Conclusions

This study presents a new way to tailor energetic material reactants toward their safer functionality. Aluminum (Al) and copper oxide (CuO) powders combined with 4 vol % carbon nanotubes (CNT) was the baseline mixture considered. Ammonium nitrate (AN) as an additive to Al+CuO+CNT was examined by replacing a portion of CuO with equal mole fractions of AN up

to 50%. This study explored low temperature AN decomposition as a mechanism to inactivate the Al+CuO+CNT+AN reaction when exposed to heating conditions simulating accidental fire. This was a proof of concept study that established a 4.0 equivalence ratio threshold when 50% of CuO is replaced with AN to cause a non-ignition after heat treatment exposure. The simulated fire conditions were achieved using a vacuum oven operating in an air environment with programmed heating at 100 degrees per minute to 230°C. Thermal chemical software was also used to predict the adiabatic flame temperature and heat of combustion pre- and post- heat treatment. Results from the simulations are in excellent agreement with the experimental observations that show unsustained propagation for reactions that produce an adiabatic flame temperature below 2000 K, an established limit for self-sustained energy propagation for energetic composites. This mechanism may be extended to higher heating rates as long as the conditions allow enough time for AN to fully decompose before the composite reaches its ignition temperature. This study is the first to explore a means to increase the fire safety of a composite energetic material in any field application.

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