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Desensitizing ignition of energetic materials when exposed to accidental fire

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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.

1. 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 vol% 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°/min [14]. In contrast, igniters in ordnance systems produce heating rates on the order of 10^6°/min [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 tunability of composite energetic materials and important for the full life-cycle safe handling of these materials.

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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. 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 μm. Aluminum (Al) powder has an average spherical particle diameter of 4.0 μm 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 mol 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.

$$3CuO + 3NH_4NO_3 + 4Al \rightarrow 2Al_2O_3 + 3Cu + 3N_2 + 6H_2O \quad (1)$$

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.

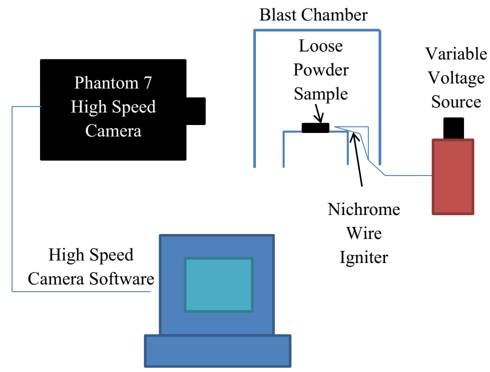

Fig. 1. Experimental setup including high speed camera, blast chamber housing sample and Nichrome wire ignition system.

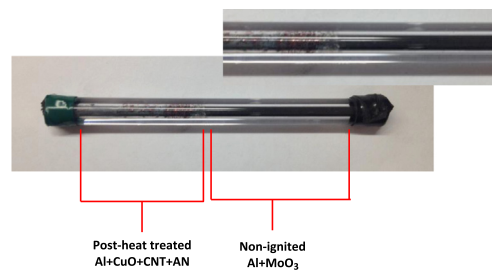

Fig. 2. Flame tube apparatus shown after an experiment in which the post-heat treated primer formulation with an ER=4.0 was ignited but did not ignite the highly ignition sensitive $Al+MoO_3$ powder thermite. An enlarged view of the tube at the junction of the two powders is shown as an inset.

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 50 mg 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.

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