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Controlling the electrostatic discharge ignition sensitivity of composite energetic materials using carbon nanotube additives

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ABSTRACT

Powder energetic materials are highly sensitive to electrostatic discharge (ESD) ignition. This study shows that small concentrations of carbon nanotubes (CNT) added to the highly reactive mixture of aluminum and copper oxide (Al + CuO) significantly reduces ESD ignition sensitivity. CNT act as a conduit for electric energy, bypassing energy buildup and desensitizing the mixture to ESD ignition. The lowest CNT concentration needed to desensitize ignition is 3.8 vol.% corresponding to percolation corresponding to an electrical conductivity of 0.04 S/cm. Conversely, added CNT increased Al + CuO thermal ignition sensitivity to a hot wire igniter.

1. Introduction

Powder composite energetic materials pose a particular threat to electrostatic discharge (ESD) ignition. These composites may be composed of solid fuel and oxidizer particles that produce exothermic reactions upon ignition. A common fuel is aluminum (Al) and can be combined with many different solid oxidizers including metal oxidizes like copper oxide (CuO) [1].

Weir et al. studied nine different composites and showed a correlation between measured electrical conductivity and ESD ignition sensitivity with Al + CuO ranking the most electrically conductive and most ESD ignition sensitive [2]. They also defined ESD ignition sensitivity as ignition below the threshold energy of 100 mJ but examined only micron-scale particle composites. This was a first step toward identifying a measurable property of the reactants, such as electrical conductivity, and linking that property to ESD ignition sensitivity.

Weir et al. in Ref. [3] extended this correlation to nano-scale particle composites and showed that aluminum combined with molybdenum trioxide (MoO_3) became significantly more ESD ignition sensitive as the Al particle size decreased. Aluminum particles inherently contain an alumina passivation shell that can range from 3 to 5 nm thick but is independent of particle size [4]. For this reason, as the aluminum particle size decreases, the inherent alumina concentration of the powder increases. Thus, there exists a trade-off between the increased surface area to volume ratio of the nano-scale particles that enhance diffusion controlled reactions versus the higher alumina concentration that can hinder energy propagation with properties that are more insulative. Weir et al. [3] showed that adding alumina to a micron-Al + MoO_3 at an equivalent concentration to a nano-Al + MoO_3 did not sensitize the mixture to ESD. But, for nano-Al particles, ESD ignition sensitivity was increased by several orders of magnitude compared to micron-Al + MoO_3 with equivalent alumina, which achieved no ignition. The interesting component of this study was that alumina that exists as a thin coating surrounding an aluminum core acts as a capacitive network and does not detract from ESD ignition, while an equivalent addition of alumina in bulk sizes on the order of 30 nm, prevents ESD ignition.

Electrostatic discharge ignition sensitivity as a function of the alumina passivation shell thickness was further examined in a study by Collins et al. [5]. Aluminum particles were synthesized with varied shell thicknesses and their response to ESD were measured in terms of ignition delay time. Thicker shells resulted in longer delay times and these results also correlated with measured electrical conductivity. Simulations were also performed using COMSOL multiphysics software and suggested the primary ignition mechanism was joule heating of the Al core as opposed to dielectric heating of the alumina shell.

The ESD ignition sensitivity of aluminum combined with polytetrafluoroethylene (PTFE) was examined by Collin et al. [6]. They

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established the feasibility of manipulating electrical conductivity of the composite by using additives such as carbon nanotubes (CNT) to control the ESD ignition sensitivity. They showed with CNT additives to Al + PTFE a narrow range of electrical conductivities (i.e., on the order of 0.0025 μS/cm) could be produced and resulted in ESD ignition [6]. They also showed Al + PTFE mixtures that were once insensitive became sensitive by controlling their electrical conductivity with the CNT additive [6].

All of these studies suggest that there exists an electrical conductivity range that spurs ESD ignition. If a composite exhibits electrical conductivities that are either too low or too high, then the electric energy may either absorb or not absorb within the composite enough to spur ignition or the electric energy may bypass the composite by channeling through an electrically conductive pathway such that energy buildup cannot happen.

The objective of this study is to examine variations in electrical conductivity and ESD ignition sensitivity for Al + CuO powders with varied CNT concentrations. A second objective is to determine how the CNT additive affects energy propagation once ignition is achieved. Percolation was determined from electrical conductivity measurements. Ignition sensitivity was evaluated using a standard ESD ignition apparatus reported in previous work [2,3,5,6]. Energy propagation was evaluated from flame speed tests using a high-speed camera and analytical software. It is noted that the findings here are specific to micron-scale Al + CuO particle composites but have implications towards ESD safety of other powder composite energetic materials.

2. Experimental

2.1. Materials

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 to 10 μm. Aluminum (Al) powder has an average spherical particle diameter of 4.0 μm and copper oxide (CuO) powder has an average spherical diameter of 50 nm. All powders were procured from Alpha Aesar (Ward Hill, Massachusetts).

2.2. Mixing procedure

The masses for the fuel and oxide powders were calculated for a stoichiometric equivalence ratio. These proportions were combined with hexanes and sonicated for a total of one minute in ten second intervals. This cyclic program prevents damage to the alumina passivation shell during the mixing process. Sonication has been shown to be effective for producing homogeneous composites [7]. The composite was then poured into a glass dish and placed in a fume hood to evaporate and the dried composite was reclaimed for further testing.

2.3. Adding CNT

The concentration of CNT varied as a function of vol.% of Al + CuO. The masses corresponding to each vol.% were determined by first calculating the theoretical maximum density (TMD) for Al + CuO, and is 5.055 g/cc. The TMD was then used to calculate the CNT concentration for varied volumetric percentages. The volume percentages and their corresponding masses can be seen in Table 1. Before addition of CNTs all mixtures started with a mass of 350 mg of Al + CuO. Most experiments required less than 50 mg of powder, such that each sample preparation provided material for multiple tests. All experiments were run in triplicate to ensure repeatability of the measurements.

Table 1
Volumetric percent and mass of CNT added to Al + CuO and effective thermal conductivity of each mixture.

Set	Vol.% CNT	Mass of CNT (mg)	k_{eff} (W/mK)
1	0	0	19.5
2	0.5	1.8	21.3
3	0.75	2.7	22.2
4	1	3.5	23.0
5	1.25	4.45	24.0
6	1.5	5.4	24.9
7	2.25	8.1	27.6
8	3.08	10.9	30.4
9	3.8	13.6	33.1
10	4.6	16.3	35.8

Included in Table 1 is an effective thermal conductivity (k_{eff}) calculation based on a weighted average estimate for the thermal conductivities of each reactant. Values for the thermal conductivity, k, for each material are: k_{Al} = 0.19 W/mK, k_{CNT} = 3000 W/mK, k_{CuO} = 72 W/mK [8]. It is noted that while the thermal conductivity of CNT is 5000 times that of Al, such small concentrations of CNT only slightly affect overall thermal conductivity.

2.4. Electrical conductivity measurements

A schematic diagram of the electrical conductivity setup is shown in Fig. 1. An acrylic channel was constructed to contain a constant mass of powder sample (i.e., 40 mg) such that the powder is positioned securely between two copper electrodes. The channel was placed inside a conductive shield to negate charges from the surroundings. A high resistance low conductance (HRLC) HR2 meter from Alpha Labs (Salt Lake City, Utah) was connected to the two copper probes. For a more accurate measurement, the shielding container was held at ground potential by connecting it to the HRLC meter, which contains a high impedance amplifier.

The HRLC can measure a wide range or resistances varying from 1.0 Ω to 2.0 TΩ. The meter passes current through the sample at voltages below 2.0 V. The current that is passed through the sample decreases by a factor of ten for each resistance settings, of which

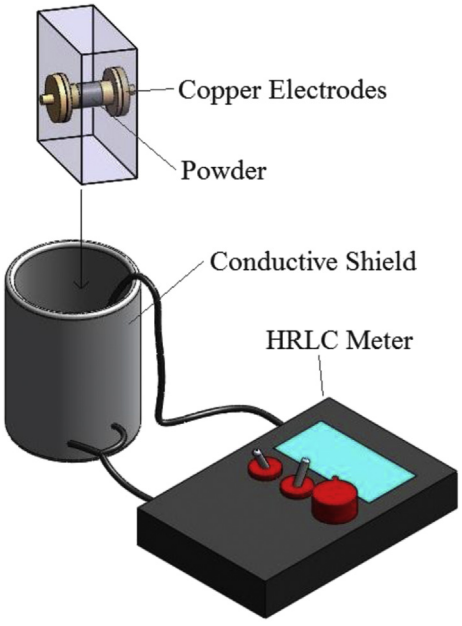

Fig. 1. Schematic of test setup for measuring electrical conductivity of powders.