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14. ABSTRACT
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Piezoelectric Ignition of Nanocomposite Energetic Materials

ABSTRACT

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Abstract: The application of piezoelectric crystals as igniters for energetic materials for power generation has not been well investigated. This study examines the voltage generation from a lead zirconate and lead titanate (PZT) piezocrystal and its ability to ignite an energetic composite composed of aluminum (Al) and molybdenum trioxide (MoO_3) nano-powder. The mechanical stimuli used to activate the piezocrystal and the ignition delay of the Al-MoO_3 composite energetic is analyzed. The mechanical compression of the crystal generates an electrical response that produces enough energy, on the order of 5 mJ, to ignite an Al-MoO_3 composite consistently and with high repeatability under 0.4 ms, which is faster than observed with thermal or shock ignition. Results show that the ignition delay times are dependent on the powder bulk density with an optimum bulk density of 50%. Composites with a bulk density lower than 50% do not produce enough particle-particle contact needed to activate ignition via electric stimuli. A comparison of ignition delay of Al-MoO_3 and voltage output from the PZT enables insight into the mechanism for electrical ignition and the use of PZT as an alternative ignition source.

TEXAS TECH UNIVERSITY
Department *of* Mechanical Engineering

December 18, 2012

Re: Manuscript for publication consideration in *Journal of Power Sources*
"Piezoelectric Ignition of Nanocomposite Energetic Materials"

Dear Editor,

Enclosed you will find our manuscript submitted for publication consideration in *Journal of Power Sources*. The authors are Eric Collins, Michelle L. Pantoya (corresponding author), Andreas Neuber, Michael Daniels, and Daniel Prentice. We have not submitted this article elsewhere at any time.

This article is a study on piezoelectric ignition of an energetic material for power generation applications. The physics governing piezoelectric ignition of energetic materials, especially for particulate composites, are scarcely reported in the literature. Also, piezoelectric igniters are becoming more widely used, especially in the ignition of fuels for fuel cells and batteries. This is a timely study on the fundamental response of nanoparticles to electrical stimuli produced by a piezoelectric crystal. Results show ignition sensitivity is a strong function of the bulk density of the composite. Microstructural features of the composite are observed to derail the path of electrical energy and prolong ignition.

These findings have relevance to anyone working with solid fuels and composites because ignition is the first step in energy generation.

Thank you for considering this manuscript.

Sincerely,

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Highlights

- Piezoelectric ignition of aluminum-molybdenum trioxide was examined
- The electrical mechanism induces joule heating through the alumina shell increasing the core aluminum to ignition.
- Bulk density influences ignition sensitivity with 50% corresponding to reduced ignition delay time and energy.
- As little as 5mJ produced by the piezoelectric stimulates ignition repeatably.

Piezoelectric Ignition of Nanocomposite Energetic Materials

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Abstract

The application of piezoelectric crystals as igniters for energetic materials for power generation has not been well investigated. This study examines the voltage generation from a lead zirconate and lead titanate (PZT) piezocrystal and its ability to ignite an energetic composite composed of aluminum (Al) and molybdenum trioxide (MoO_3) nano-powder. The mechanical stimuli used to activate the piezocrystal and the ignition delay of the Al-MoO_3 composite energetic is analyzed. The mechanical compression of the crystal generates an electrical response that produces enough energy, on the order of 5 mJ, to ignite an Al-MoO_3 composite consistently and with high repeatability under 0.4 ms, which is faster than observed with thermal or shock ignition. Results show that the ignition delay times are dependent on the powder bulk density with an optimum bulk density of 50%. Composites with a bulk density lower than 50% do not produce enough particle-particle contact needed to activate ignition via electric stimuli. A comparison of ignition delay of Al-MoO_3 and voltage output from the PZT enables insight into the mechanism for electrical ignition and the use of PZT as an alternative ignition source.

Key Words: Aluminum, Ignition, Combustion, Piezocrystal, Nanoparticles, Thermites

1. Introduction

Piezocrystals are commonly used in fuel cell applications. For example, Ma et al. [1] used a PZT as an actuator in a proton exchange membrane fuel cell that showed the PZT compressed more air into the catalyst layer enhancing electrochemical reactions, resulting in higher current output. For miniaturized applications, direct methanol fuel cells (DMFC) incorporated a piezoelectric valveless micropump as the fuel delivery system and established the feasibility of DMFC in power electronics applications [2]. Energetic materials are also being considered for MEMS applications and one key commonality for MEMS based power generation is the use of aluminum as the fuel [3]. Aluminum is also a common component of fuel cells and batteries [4-6]. With much research investigating micro-propulsion and power systems that utilize both aluminum and piezocrystals, there is only scarce reporting on piezocrystals as igniters for aluminized energetic materials.

Some studies involving piezocrystals and a solid energetic material utilized the detonation of an explosive to transfer shock wave energy into a piezocrystal disc, thereby using the piezocrystal as a ferroelectric generator [7–9]. The physics governing electrical ignition of solid energetic materials is uniquely different from other forms of ignition stimuli. Understanding piezoelectric ignition is paramount for the development of advanced igniters for miniaturized propulsion systems, micro-thrusters and mobile robotics. The objective of this study is to examine a piezoelectric material as the ignition source for a solid composite energetic material. This objective will be accomplished by characterizing a piezocrystal's electrical response to mechanical stimuli and coupling these characterizations with the energetic material's ignition sensitivity resulting from the electrical energy generated by the piezocrystal.

The piezocrystal used here and in [7] is a mixture of lead zirconate and lead titanate, also known as PZT. This is a frequently used piezocrystal for ignition of hydrocarbon fuels and is commonly found in propane fueled gas igniters [10, 11]. The energetic composite is a mixture of aluminum (Al) fuel particles combined with molybdenum trioxide (MoO_3) flakes. Ignition of this particular mixture has been well documented, including ignition by thermal and shock stimuli. For example, Al-MoO_3 was shown to have an ignition delay on the order of 20 ms when thermally ignited by a 50 W CO_2 laser [12] and 0.42 ms when ignited by a reflective shock [13]. In this way, comparison of Al-MoO_3 PZT ignition sensitivity enables insight into the mechanism for electrical ignition and the use of PZT as an alternative ignition source.

2. Experimental

The experimental setup is comprised of a piezoelectric crystal whose top and bottom, see Fig 1(a), are electrically connected to two opposing copper electrodes, see Fig. 1(b). A 0.8 kg drop weight with variable drop height serves to apply pressure to the PZT and is held in place within a dielectric drop tube resting on a conducting support. The electric charge released by the PZT is monitored with a high-speed current probe and a high voltage probe is utilized to monitor the potential of the developing discharge in the electrode gap filled with Al-MoO_3, cf. Fig. 1(b). Ignition of the powder is witnessed through the sharp increase in luminosity detected with a photodiode. The simultaneous current and voltage measurement along with the luminosity enabled determining ignition sensitivity quantified in terms of ignition delay time and ignition energy.

The composition examined consists of 80 nm average diameter spherical Al particles and 380 nm MoO_3 flakes. The Al and MoO_3 powders were mixed using a sonification procedure described in detail elsewhere [14]. After mixing, the powders were loaded into a channel with a

volume of 0.03cm^3. The copper electrodes were loosely attached to the ends of the channel which allowed the products from the reaction to push electrodes and escape out the ends of the channel. The bulk density of the powder in the channel varied and was calculated as a percentage of the theoretical maximum density:

$$TMD = \frac{1}{\sum_{j=1}^{n} \frac{\%M_j}{\rho_j}}, \qquad (1)$$

where %M is the percent of mass within the mixture, ρ is the density of the material, and the index of summation (j) represents the materials contained in the mixture, and the upper bound of summation (n) is the total number of materials contained in the mixture. The TMD for Al+MoO_3 was calculated to be 3.91 g/cc.

The height of the drop weight above the PZT was varied from 9.5 to 19.7 cm to provide a range of voltage output from the PZT. As expected the peak voltage from the PZT into an open circuit increased as the drop height increased. Initial tests were performed on the PZT using an air gap as the reference condition. As the weight dropped on the PZT when connected to a circuit with air as the medium between the 0.5 cm gap, the voltage amplitude increased on a millisecond timescale until the voltage potential between the electrodes caused the electric field to exceed the dielectric strength of air and a spark was produced. When the spark bridged the gap, the voltage collapsed on a sub-microsecond timescale and a distinct current pulse is observed in this case, see Fig. 2(a). For a spark gap distance of 0.5 cm, the voltage output for all drop heights was repeatable with an average value of 4.9 kV and a variation of 7%. Characterizing the PZT aided in understanding the energetic material response to mechanical input and electrical output produced by the PZT.

3. Results and Discussion

The air gap within the 0.03 cm^3 volume channel was replaced with Al+MoO_3 powder. The mixture was ignited using the PZT to create a spark between the two electrodes as shown in Fig. 1(b). As the spark ignited the powder, the high speed photo diode captured the luminosity from the reaction [Fig. 2(c)]. The length of time between the spark and the time when luminosity reached a threshold of 0.1 V was recorded as the ignition delay of the reaction. The bulk densities of Al+MoO_3 in the channel were 20%, 40%, 50%, and 60% TMD. Figure 3 shows the average voltage output with respect to average ignition time delay for each of the bulk densities. The bars indicate standard deviations from approximately 15 measurements.

The results in Fig. 3 represent the voltage and time delay average and their standard deviation for all tests at each bulk density. The delay time from spark ignition is significantly faster than delay times reported for thermal ignition (e.g., 20 ms) [10, 12] and similar but slightly faster than for reflected shock ignition (e.g., 0.42 ms) [11,13]. The delay time varied for the tests that produced voltages between 2-4 kV and was generally > 0.1 ms. However, as the voltage increased to more than 5 kV, the time delay was $\leq$ 0.1 ms. Figure 3 suggests the optimal bulk density is 50% of TMD where delay time is the fastest and voltage is the highest. The powder with a bulk density less than 50% of TMD does not have as much particle-particle contact as the 50%, and the powders with a bulk density of 60% of TMD may be compressed with enough force to create fractures, cracks and deformities within the composite that could influence the electrically stimulated ignition mechanism. Pantoya et al. showed via scanning electron microscopy that Al+MoO_3 compressed to 35% TMD produced no cracking or apparent damage to particles but compressed to 75% TMD resulted in significant fractures and cracking of MoO_3 [14]. It is also noted that the voltage with air as the medium in the spark gap had a steady value

of 4.9 kV and the voltage with the powder as the medium varied from about 2 – 7 kV. This variation in voltage is dependent on the dielectric strength of the medium, which is a function of the arrangement of particles within the powder. Obviously, the 50% TMD had the highest dielectric strength, leading to the largest potential build-up before spark ignition.

Studies on thermal ignition of Al-MoO_3 show significant variation of ignition delay time with variations in density. Lower density powders tend to form hot spots that develop more prominently in highly porous (loose powder) media igniting the mixture at reduced ignition delay times than consolidated media [15]. For impact ignition, increasing the bulk density corresponds to a decrease in ignition sensitivity [16]. In impact ignition, breaking or damaging the Al passivation shell is a rate limiting step for ignition, such that highly consolidated mixtures contain higher stresses on individual particles due to the forced contact between particles, spurring ignition more readily for highly consolidated mixtures [16].

Research has shown a correlation between electrical conductivity and electrostatic discharge ignition sensitivity in these composites [17]. Specifically, the mechanism for electrical ignition in aluminum fueled energetic composites involves joule heating of the highly resistive alumina passivation shell that creates a heating blanket surrounding the Al core and spurring ignition of Al [17]. Oxidizers that are more electrically conductive are also more electrostatic ignition sensitive, and Al-MoO_3 has a relatively high electrical conductivity in comparison to other Al based composites [17]. This mechanism is applicable in PZT ignition since the stimulus is electrical. In this way, the electrical energy is absorbed in the alumina shell, converted to joule heating and thereby ignites the Al particle.

The power (P), or rate at which the energy was delivered to Al-MoO_3, was calculated from the voltage-current product, $P = I * V$. The duration of significant power delivered to the

mixture was on the time scale of about 200 ns, which is also the duration of the current bridging the electrode gap through the spark as shown in Fig. 2(b). The power was numerically integrated to approximate the energy delivered to the Al-MoO_3.

The time delay trend lines in Fig. 4 indicate that more energy is injected into the powder with 50% TMD. In absolute terms, the energy output to ignite the powder is small, approximately 3-10 mJ. These results imply that ignition of the energetic composite is not significantly altered by the energy released from mechanical compression of the PZT. At the input energies studied here, the PZT produces enough electrical energy to stimulate ignition, regardless of drop height (and potential energy) compressing the PZT.

4. Conclusion

These results show that a solid energetic composite can be ignited by a piezocrystal generated current pulse and the mechanism for ignition is consistent with electrical stimuli. Results show ignition delay times are dependent on the powder bulk density with an optimum bulk density of 50% TMD. Higher TMD promotes cracking within the composite microstructure that inhibits ignition and lower than 50% TMD may not produce ideal particle-particle contact needed to spur ignition. Via the piezoelectric effect, the mechanical compression of the crystal generates an electrical response that produces enough energy, on the order of 5 mJ, to ignite an Al-MoO_3 composite consistently and with high repeatability under 0.4 ms, which is faster than observed with thermal or shock ignition. This observation may be a result of the electrical mechanism for ignition in Al based energetic materials. Specifically, electrical energy absorbed by the highly resistive alumina shell promotes joule heating of the alumina and triggers ignition of the Al core.

Acknowledgements

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Figure Captions

Figure 1. (a) Piezocrystal drop test setup for ignition of Al-MoO_3 powder. (b) Electrical circuit.

Figure 2. (a) Voltage and current as spark from PZT bridged 0.5 cm air gap. (b) Voltage and current as spark from PZT bridged gap filled with powder. (c) Time delay between spark and luminosity from photo diode.

Figure 3. Voltage output from the PZT as a function of time delay of the Al+MoO_3 reaction with standard deviations represented by bars.

Figure 4. Trend lines for total energy from the PZT as a function of time delay.

Figure(s)

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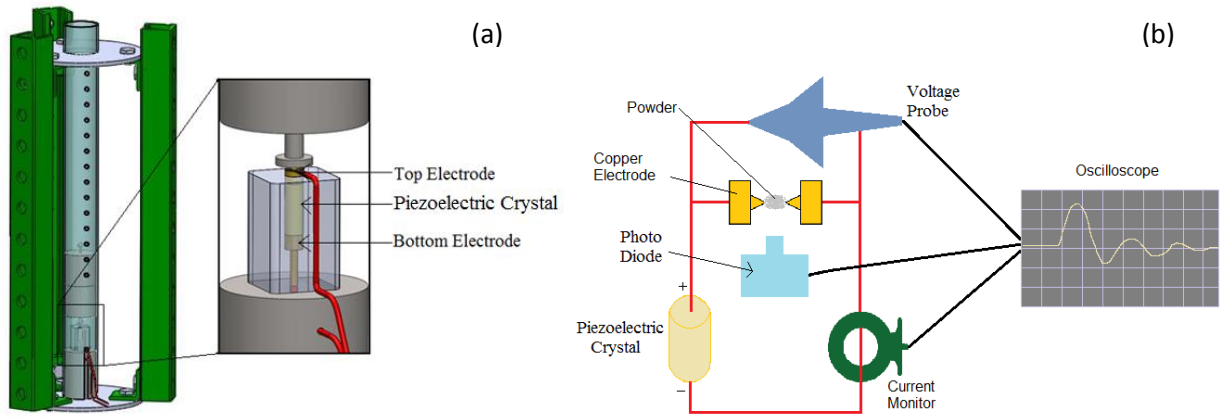

Figure 1. (a) Piezocrystal drop test setup for ignition of Al-MoO_3 powder. (b) Electrical circuit.

Figure(s)

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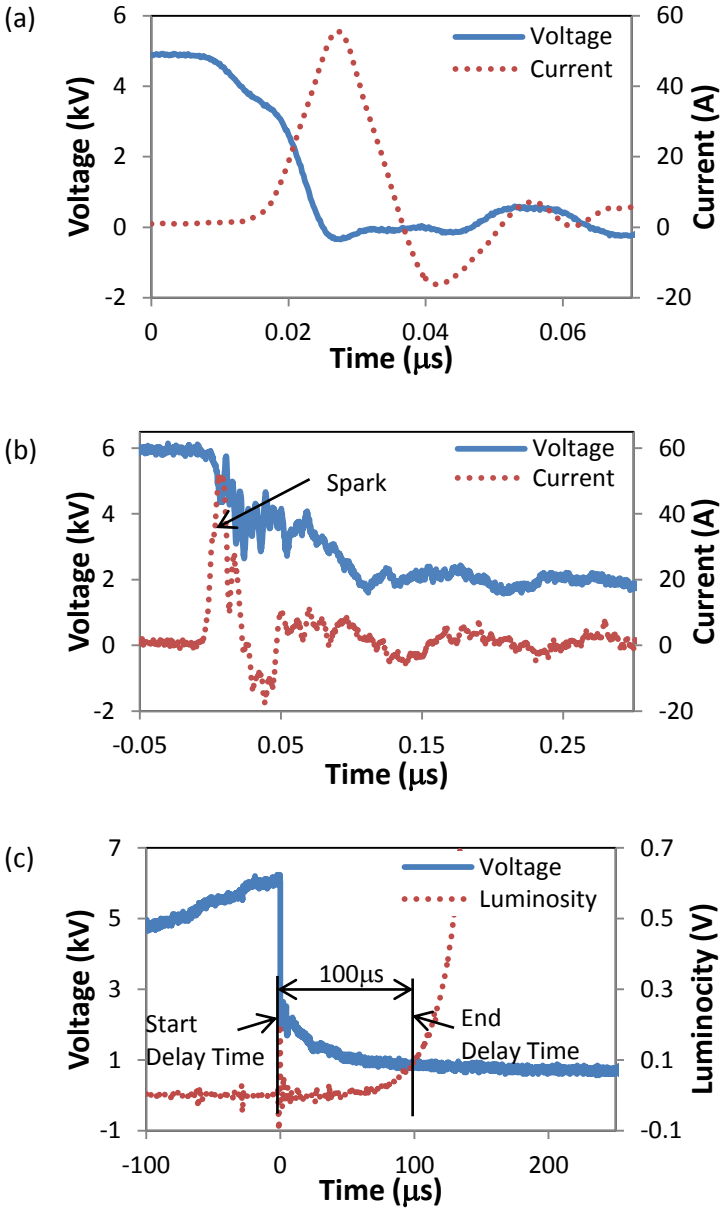

Figure 2. (a) Voltage and current as spark from PZT bridged 0.5 cm air gap. (b) Voltage and current as spark from PZT bridged gap filled with powder. (c) Time delay between spark and luminosity from photo diode.

Figure(s)

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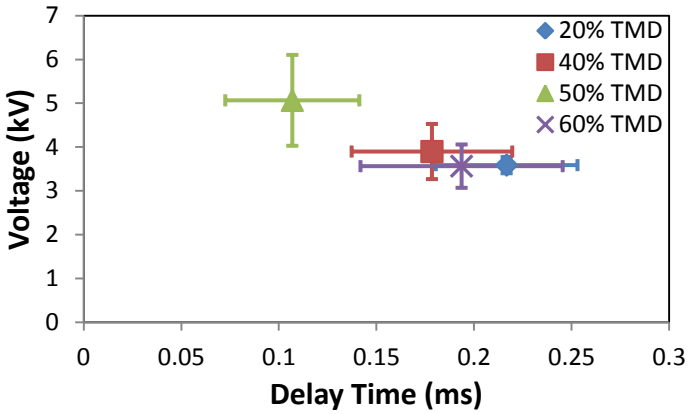

Figure 3. Voltage output from the PZT as a function of time delay of the Al+MoO_3 reaction with standard deviations represented by bars.

Figure(s)

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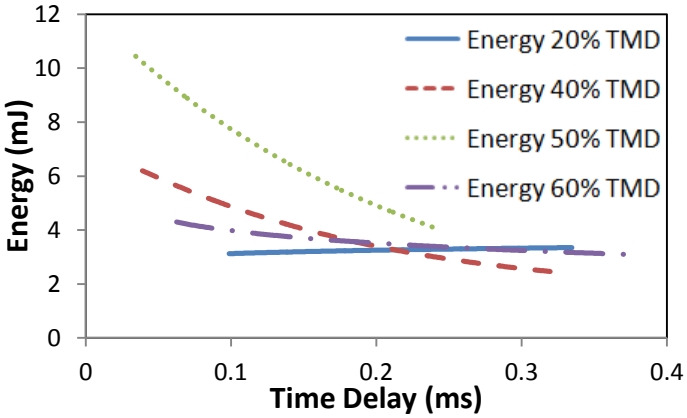

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