Using laser-driven flyer plates to study the shock initiation of nanoenergetic materials

W L Shaw\textsuperscript{1}, R A Williams\textsuperscript{2}, E L Dreizin\textsuperscript{2} and D D Dlott\textsuperscript{1}

\textsuperscript{1}School of Chemical Sciences, University of Illinois at Urbana-Champaign, 600 S. Mathews Ave., Urbana, IL 61801;
\textsuperscript{2}Newark College of Engineering, New Jersey Institute of Technology, University Heights, Newark, NJ 07102.

Email: dlott@illinois.edu

Abstract. A tabletop system has been developed to launch aluminium laser-driven flyer plates at speeds of up to 4 km/s. The flyers were used to initiate nanoenergetic reactive materials including aluminium/iron oxide and aluminium/molybdenum oxide thermites produced by arrested reactive milling. The flyer flight and impact was characterized by photon Doppler velocimetry and the initiation process by time-resolved emission spectroscopy. Impact initiation thresholds were determined for 50 µm thick flyer plates producing 10 ns shocks. The intensities, delays and durations of the emission bursts, and the effects of nanostructure and microstructure on them were used to investigate fundamental mechanisms of impact initiation.

1. Introduction

Our recently developed \cite{1} laser-driven flyer plate apparatus is capable of studying impact initiation of reactive materials in quantities of micrograms or less \cite{2}. This allows us to analyze the dynamics of reactive nanomaterials being developed before large-scale fabrication is available. By studying materials during the early stages of reaction, we can probe reaction kinetics and dynamics of shock initiation, and observe condensed phase reactions before significant gas-phase products form.

Our intent is to better understand fundamental mechanisms in condensed phases, where the initial stages of reaction are believed to involve oxygen transfer from metal oxide to metal \cite{3}, using time-resolved spectroscopy. When a reactive material is initiated, it emits an intense burst of light. For a large explosive charge, the emission burst duration will be representative of the rate of reaction propagating through the charge. For instance Thadhani and co-workers observed energy release from impacted thermite powders occurs on the 100 µs time scale \cite{4}. But with the tiny bits of material used here, emission burst durations will be reflective of nanoscale mass-transfer and chemical kinetics. We will show here that impact-induced reactions of individual thermite particles can occur on the 50 ns time scale.

Recent developments in materials science have allowed for the fabrication of composite thermites with nanoscale interleaving layers of metals and metal oxides \cite{5}. These nanocomposites exhibit increased ignition reaction rates, lower ignition temperatures, and greater shock sensitivity compared to their micron grain size counterparts \cite{4,6}. One method for fabrication, arrested reactive milling (ARM), has proven to be a useful process for producing micron size particles $<1$ µm to $>60$ µm, with grain sizes of 100 nm or less \cite{7,8}. In this study, we use laser-driven flyer plates to investigate shock induced initiation of $\text{Fe}_2\text{O}_3 + 4\text{Al}$ and $\text{MoO}_3 + 8\text{Al}$ thermites produced by ARM.
2. Experimental

The apparatus for launching laser-driven flyer plates has been described previously [1]. Its key components were a Nd:YAG laser (10 ns, 2.5 J) to drive the flyer plates, a diffractive-optic (Silios, Corp.) to homogenize the beam into a top hat profile, and a photonic Doppler velocimeter (PDV) to monitor flyer plate velocities. The aluminum flyer plates used here were 50 µm thick and produced 10 ns duration planar impacts over an estimated 160 µm diameter region in the center of the flyer [1]. They were 700 µm in diameter and were launched across 375 µm gaps to allow launch reverberations in the flyers to damp away prior to impact. The sample chamber was evacuated to 500 mtorr vacuum to eliminate effects of air compression by the flyers.

2.1. Thermite Samples

The thermites used here were Fe$_2$O$_3$ + 4Al and MoO$_3$ + 8Al. These nanocomposite thermite powders were prepared by ARM, as described elsewhere [7,8]. The resulting thermite particles were fully dense, ranging in size from 0.75 to 75 µm. They consisted of nanoscale oxide inclusions uniformly distributed in an aluminum matrix.

The samples were prepared by spreading a thin layer of cement on a glass window and then sprinkling a small amount of thermite powder onto the cement. A UV curable acrylic glue (Dymax, UV weld) was spin-coated onto a ¼” thick, 2” x 2” BK7 window (Chemglass) to produce a 0.75 µm thick cement layer. After the thermite powder was sprinkled, the cement was UV-cured. The samples were inspected with a microscope to insure that the thermite particles had not reacted from exposure to UV radiation or heating during the curing process.

2.2. Optical System

The apparatus for collecting sample emission bursts is depicted in figure 1a. A 10x microscope objective (Nikon, LU Plan Fluor) was used to collect the thermite emission and PDV signals reflected from the flyer plates. A dichroic mirror (Semrock, FF875-Di01) set to a 30 degree angle reflected 300-900 nm while transmitting the 1550 nm PDV beam. The PDV beam was larger than the thermite particles, which allowed PDV to monitor the speed profile of the laser-driven flyer plates as they approached and impacted the particles and the glass window (figure 1).

We viewed the thermite particles on the glass windows in situ using a homemade microscope, as depicted in figure 1. An expanded image of the particles was created using a 25 cm achromatic doublet lens. A variable iris was placed in the image plane, and a drop-in mirror transmitted this image to a video camera equipped with magnifying optics. By looking at the video image, we could translate the sample and close down the iris until we were observing only a single size-selected particle. By calibrating the image with a reticle with 10 µm divisions, the particle size could be measured. In the present experiments, we selected only 60 ± 5 µm diameter particles for observation, and only particles that were more than 150 µm distant from the other particles. Once a particle was selected and the image irised down to minimize the observation of the surrounding cement, the drop-in mirror was removed, and the emission was directed to a fast (< 1 ns) photomultiplier tube (Hamamatsu, H10720-20) connected to an 8 GHz digitizing oscilloscope.

As illustrated in figure 1b, the particles have irregular shapes. Since we only observed the opaque particles in the plane of the glass window, the particle heights were unknown. While the particles studied all had similar diameters, there may be substantial variations in heights.

3. Results

Correlated photomultiplier tube and PDV signals can be seen in figure 2. Time zero is when the flyer plate impacts the window. Figure 2a shows the emission observed by the photomultiplier tube. Figure 2b contains the velocity history of the flyer plate. This plot is created through a short-time Fourier transform (STFT), also known as a moving-window Fourier transform, of the raw signal detected by the PDV using a 160 MHz window and equation (1).
flyer velocity) = (measured frequency) * (wavelength/2)                       (1)

The STFT used in this analysis results in 1 ns of time uncertainty for events observed by PDV. It can be seen from the velocity history that there is a slight delay between the impact of the flyer plate in figure 2b and the emission observed in figure 2a. It is important to note that the PDV cannot observe the flyer plate through the thermite particles. This makes the time of impact determined by the PDV system that of the flyer plate impacting the glue and glass window. Since the thermite particles project above the glue and glass surface, the flyer plate has contacted the hidden part of the particle some undetermined amount of time before time zero.

Emission bursts detected over a 100 ns time interval after a laser-driven flyer plate impacted individual 60 µm thermite particles are displayed in figure 3 at several flyer plate speeds. Time zero is the instant of flyer plate impact with the glass window, as determined using PDV velocity histories of each shot. The light burst intensity profiles were digitized for 20 µs to insure we did not miss any slower light emissions. In control experiments, we observed that the emission from impacted cement and glass was much smaller than what we show in figure 3. The thermite emission profiles consisted of two bursts of light. The first was a sharp spike coinciding closely with the impact of the flyer plate. It was followed by a delay of ~500 ns and a second much weaker emission burst, which lasted for a few microseconds (not shown). The secondary emission was similar for both thermites, and will not be discussed further here. One can see from figure 3 there is a threshold impact speed above which the thermite emission intensities increase dramatically. This threshold for MoO$_3$ + 8Al was lower than for Fe$_2$O$_3$ + 4Al. MoO$_3$ + 8Al also had slightly longer duration emission bursts. At 0.8 km/s the emission burst onset delay was longer for MoO$_3$ + 8Al, but at higher impact speeds the delays for both thermites became much shorter and were about equal.

To determine integrated emission intensities independent of small changes in the emission burst shape, we integrated each emission burst across the intensity points 10% above the baseline. Figure 4a shows the integrated intensities at different flyer speeds. Each point was the average of three shots, and the error bars were one standard deviation. We can gain a sense of the dynamics involved by looking at this plot. MoO$_3$ + 8Al nanothermite exhibits a lower velocity threshold than Fe$_2$O$_3$ + 4Al.

The delay between flyer impact and the initial 10% rise of the emission curves is plotted in figure 4b. The emission burst durations, measured as the time interval between 10% points of the emission bursts, are plotted in figure 4c. The emission burst durations were interpreted as arising from the rates of chemical reactions of the thermite particles. Both MoO$_3$ + 8Al and Fe$_2$O$_3$ + 4Al thermites exhibited onset delays of ~15 ns below 1.0 km/s. Above 1.0 km/s the onset delays were reduced to ~5 ns and the delays became independent of flyer speed. Below 1.0 km/s, the emission burst durations from
MoO$_3$ + 8Al were significantly longer (60 ns) than for Fe$_2$O$_3$ + 4Al (20 ns). But as the impact speeds increased, both types of thermites had about the same emission burst duration of ~20 ns.

4. Discussion
Both types of thermites, when impacted at lower speeds (e.g. 0.8 km/s) produce weaker emission bursts after a ~15 ns delay. We note that 15 ns is about the expected shock transit time through a 60 μm particle based on an acoustic wave traveling through aluminum. Our tentative interpretation of the emission at these lower speeds is that it represents thermal emission or triboluminescence of the shocked thermites. As the impact speed was increased, both types of thermites showed a threshold for much more intense emission bursts occurring with minimal delays. We interpret these increased-intensity bursts are arising from exothermic chemistries in the condensed phase. The emission burst onset delay when the higher-intensity bursts were observed was minimal, but it is difficult to interpret these delay values due to the time delay between flyer impact with the hidden back part of the thermite particles and the flyer impact with the glass window. However, it is clear that the impact speed threshold for the higher-intensity bursts was lower for the MoO$_3$ + 8Al thermite (~1.9 km/s) than for the Fe$_2$O$_3$ + 4Al thermite (~2.6 km/s). It is also clear that the emission burst durations for the MoO$_3$ + 8Al thermite were consistently longer than for the Fe$_2$O$_3$ + 4Al thermite.

In this study, we have described a novel apparatus for studying the fundamental mechanisms of impact initiation of reactive nanomaterials using time-resolved spectroscopy. We have shown that we can obtain excellent signals corresponding to the impact-driven emission bursts from small thermite particles, and we can accurately characterize the intensity and duration of these bursts. Here we presented preliminary data obtained with a few tens of impact events, which suggests that a more extended investigation of these phenomena could be very interesting. We need to obtain better statistics on flyer plate speed dependences, and also study the effects of different shock durations by

---

**Figure 3.** Emission bursts from shocked single 60 μm thermite particles at the indicated flyer speeds. Time zero was when the flyer plate impacted the glass window.

**Figure 4.** (a) Intensities of thermite emission bursts. (b) Time delay between flyer impact, measured by PDV, and emission burst onset. (c) Duration of single particle emission bursts.
varying the thicknesses of the flyer plates. We wish to study the effects of thermite particle size in order to better understand the impact delay phenomenon. We also need to spectrally resolve the emission bursts, and we are developing a better and more-sensitive detection system for such measurements. We plan in the future to extend these studies to multiple-particle aggregates, in order to better understand how reactions spread among adjacent particles. In any case, we believe we have convincingly demonstrated that our novel laser-driven flyer apparatus is well-suited to these investigations.

Acknowledgments
The research described here was based on work supported by the US Army Research Office under awards W911NG-13-0217 (DDD) and W911NF-12-1-0161 (ELD), and the US Defense Threat Reduction Agency (DTRA) under award HDTRA1-12-1-0011 (DDD). William L. Shaw acknowledges support from the Stewardship Sciences Academic Alliance Program (Carnegie-DOE Alliance Center) under award DE-NA002006.

References
[1] Brown K E, Shaw W L, Zheng X X and Dlott D D 2012 Rev. Sci. Instrum. 83 103901-13
[2] Zheng X X, Curtis A D, Shaw W L and Dlott D D 2013 J. Phys. Chem. C 117 4866-75
[3] Dlott D D 2003 Energetic materials vol 2, ed P Politzer and J S Murray (Amsterdam ; Boston: Elsevier) pp125-179
[4] Cheng J L, Hng H H, Lee Y W, Du S W and Thadhani N N 2010 Combust. Flame 157 2241-9
[5] Dreizin E L 2009 Prog. Energ. Combust. 35 141-67
[6] Hunt E M, Malcolm S, Pantoya M L and Davis F 2009 Int. J. Impact. Eng. 36 842-6
[7] Schoenitz M, Ward T S and Dreizin E L 2005 Proceedings of the Combustion Institute 30 2071-8
[8] Umbrajkar S M, Seshadri S, Schoenitz M, Hoffmann V K and Dreizin E L 2008 J. Propul. Power 24 192-8