Microstructural effects on the ignition behavior of HMX

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Abstract. The detonation physics community has embraced the idea that initiation of high explosives proceeds from an ignition event through subsequent growth to steady detonation. A weakness of all the commonly used ignition and growth models is that microstructural characteristics are not explicitly incorporated in their ignition and growth terms. This is the case in spite of a demonstrated, but not well-understood, empirical link between morphology and initiation of energetic materials. Morphological effects have been parametrically studied in many ways, with the majority of efforts focused on establishing a tie between bulk powder metrics and ignition of the compacted material. Computational efforts have defined frameworks that may be used to describe shock loaded or ignited energetic microstructures [2-4]. Recently, there has been progress in

1. Introduction

Shock to detonation transitions occurring within explosive material have generally been described as a process that proceeds from an ignition event through subsequent growth and culminates in a steady detonation. This construct is the basis for the well-known Lee-Tarver reactive flow model [1]. A weakness of all the commonly used ignition and growth models is that microstructural characteristics are not explicitly incorporated in their ignition or growth terms. This is the case in spite of a demonstrated, but not well-understood, empirical link between morphology and initiation of energetic materials. Morphological effects have been parametrically studied in many ways, with the majority of historical efforts focused on establishing a tie between bulk powder metrics and ignition of the compacted material. Computational efforts have defined frameworks that may be used to describe shock loaded or ignited energetic microstructures [2-4]. Recently, there has been progress in

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establishment of experimental techniques that enable the characterization of microstructures of pressed beds of energetic materials in order to understand the underlying mechanisms governing ignition [5, 6]. This paper describes the investigation and initial conclusions drawn by studying Class III and V HMX. We have assessed the utility of using a modified James’ model [7] as a tool to quantify the effects of bed microstructure on continuum level ignition behavior. The long term objective of this work is to assist in the future validation of modeling and simulation efforts focused on understanding microstructural or mesoscale effects on reactive systems. We hope to determine if the construction of continuum models that incorporate forms that may be parameterized using microstructural information is possible.

2. Energetic materials
HMX was chosen for this study because the length scales of one dimensional ignition behavior were achievable using our electric gun experimental platform. This assertion will be further explained later in this paper. An additional motivation for use of HMX is the significant body of information in the literature, which will facilitate future analysis, modelling, and simulation activities. Class III and V HMX materials were evaluated in this study where the lot numbers are BAE10K071-101 and BAE13E082-097 respectively. Scanning electron micrographs of the two HMX materials are shown in figure 1. A significant difference in bulk powder particle sizes exists between the two materials where remnants of this will be seen in the two dimensional cross sections of the pressed beds to be discussed in the next section. This significant change in particle character is clear when examining the two SEM images show in figure 1. The work reported here utilized samples pressed to bulk densities of 94% theoretical maximum density (TMD).

3. Microstructure characterization and image analysis
Freestanding right circular cylinder pellets with a nominal bulk density of 1.79 gm/cm^3 (94% TMD), were pressed from each of the HMX powder lots in this study. The pellets used for microstructure characterizations were 2 mm in diameter by 1 mm tall. The internal microstructure of these pellets was then characterized by Ar-ion cross-sectioning and subsequent electron microscopy. This technique was first used on explosives by Wixom et al. [6] to examine the microstructure of hexanitrostilbene (HNS) pellets. In that work, Wixom et al. also used focused ion beam (FIB) nanotomography. In the future, we expect to assess the viability of applying the FIB technique to our samples. Another option considered was x-ray computed tomography, but at this time even the highest resolution instruments cannot resolve the smaller voids in our samples. One drawback of the Ar-ion cross-sectioning technique is that the data is only two-dimensional. However, using the principles of stereology, one can still obtain valuable three-dimensional data and the quality of the subsequent electron microscopy is a major advantage of using our chosen technique.

The HMX samples were cross-sectioned with a JEOL Cross Section Polisher that uses a broad Ar beam at voltages between 2-8 kV. A mask is used to define a portion of the sample to be protected and a portion to be milled away. For the HMX samples in this study, we typically used a higher voltage (5-6 kV for >9 hours) polish to remove several hundred microns of material, then followed up with a lower voltage (3 kV for 6-9 hours) “fine” polish where we removed only 10-20 µm of material.
The cross sections were then coated with a few nm of Ir and imaged using a Zeiss Supra 35 SEM. As with other molecular crystal explosives, HMX is relatively susceptible to electron-beam damage and charging. As such, SEM imaging was performed at low voltages, ∼1-2 kV, which also ensured that we imaged only the surface of the cross section and not farther into the material. Figure 2 shows two cross-section electron micrographs and images of the corresponding loose powder for two HMX samples. The Class III powder is characterized by large particles sizes, >100 µm, and the consolidated pellets have large fully-dense grains that separate regions of porosity. The void space in this material is primarily from an extended crack network that separates the large grains. This is in contrast to the Class V material, which consists of much smaller particles. The resulting Class V pellets have a few visibly intact grains with dimensions of tens of microns, and the void space in this sample primarily comes from sub-micron porosity, that in comparison to the other sample is more uniformly distributed. As such, the average spacing between pores is small, and the Class V sample does not appear to have the large extended cracks present between grains, as in the Class III sample. These microstructural differences can be correlated to differences in the initiation properties, which will be discussed in the following section of this report.

To aid in analysis, the grayscale SEM images were enhanced to increase contrast and eliminate as much random detector noise [8] as possible. To achieve this, we utilized an adaptive Wiener filter with a 3 × 3 pixel neighborhood, which preserved the edges of the void structure. All of the images were processed using the image processing toolkit (version 8.1) in MatLab (version 8.0.0).

The filtered images were segmented by applying a threshold, where a gray-level is chosen and pixels above and below are set to 1 and zero respectively. In our images, the HMX material has lighter grayscale tones while the voids appear black. Determination of the threshold value was automated to eliminate user bias. The automation runs through the grayscale from darkest to lightest tones while monitoring the number of pores, which trends at a linear rate initially. When the gray-level approaches the tone of HMX the number of pores grows exponentially due to false void detection. The threshold is chosen just prior to the exponential rise in void count. Figure 3 illustrates the above described image analysis. Note that the subsequent analysis was performed on a Class III and V image with the same field of view. It is important to note that there is a trade-off between properly resolving bed features and capturing a representative sample set. Therefore, our assessment is preliminary and
future work will include analysis on images using an optimized field of view or correlated data sets that span multiple fields of view.

Microstructural analysis was performed on the segmented images, where black represents voids and white is the HMX. The results of four calculations are presented below in Table 1: interfacial area, percent TMD, percent difference of interface areas and interfacial area. Using the well-established principles and assumptions of stereology (uniform and random sampling) [8, 9], the surface area per unit volume ($S_v$) was calculated as

$$S_v = \left( \frac{4}{\pi} \right) \cdot L_A$$

where $L_A$ is the interface length per unit area. The density, reported as a percentage of TMD, was calculated taking the ratio of segmented solid and total image area. Table 1 reports the average density and interfacial area for Class III and V HMX materials. The value in parentheses represents the standard error of varying the segmentation threshold plus/minus two (sample size of 5). This range represents a large change (40%) in the number of voids detected, and is well into the knee of the exponential growth discussed above. In [6], Wixom et al. have compared densities and surface areas of an explosive pellet obtained via planar cross-sections and the above stereological relations to three-dimensional data obtained via FIB nanotomography and demonstrated excellent agreement.

**Table 1.** Mean values for percent TMD, interface area, and interfacial area. The value for interfacial area was obtained using a $\beta$-polymorph density of 1.91 g/cm$^3$ [10]. Values in parentheses are standard error of the mean.

| HMX Type | %TMD   | Interface Area | % Difference Interface Area | Interfacial Area |
|----------|--------|----------------|-----------------------------|------------------|
|          |        | [nm$^2$/nm$^3$] |                             | [m$^2$/g]        |
| Class III| 92.59 (0.15) | 0.001653 (0.000029) | -47                      | 0.866 (0.015)    |
| Class V  | 91.86 (0.17) | 0.003101 (0.000048) | 0                        | 1.62 (0.02)      |

Lastly, the Euclidean distance maps, figure 4, represent the distance from every pixel to the nearest void, where voids are white. The data in these maps were then binned into 100 equally spaced bins, excluding void pixels, to compare the distance distribution for each HMX material.

**Figure 4.** (Left) Distance distribution for the Class III and V HMX. Data is binned in 100 equally spaced bins. Void pixels are excluded. (Right) For distance maps, white pixels are the void regions and the blue regions are where the distance to the nearest void is the greatest, interpreted as cold spots.

4. **Ignition studies**

Experiments were conducted utilizing the two HMX materials to determine ignition behavior as a function of shock pulse thickness and amplitude. The experiments were designed to specifically probe the thin-pulse ignition regime. In order to probe the ignition behavior, an Electric Gun (E-Gun) was used to generate plate impacts with variable shock amplitude and pulse duration at a fixed spot size.
To clarify terminology, we are differentiating between ignition and general initiation events, which include ignition processes. We further specify ignition events as noted in the below numbered list to differentiate between successful ignition and insults that results in chemical reactions that will not grow to a sustainable detonation wave.

1. **Sub Critical Ignition Condition** – a shock in the explosive that generates chemical reaction but fails to propagate because the ignition process in the explosive is insufficiently sustained by the input shock to overcome energy loss to the system.

2. **Critical Ignition Condition** – a shock in the explosive that generates sufficient chemical reaction such that this event is at the threshold of sustainable reaction once input shock energy/power is depleted from the source. This ignition process will result in a successful initiation process given appropriate length scales are present within the explosive. For our experiments, this point represents a condition of 50% probability of ignition identified during threshold studies.

3. **Super Critical Ignition Condition** – a shock in the explosive that exceeds the Critical Ignition Condition. An example would be a flyer impact where the shock amplitude and duration driven into the explosive exceeds that required to Critically Ignite the material but does not necessarily sustain the growth process all the way to completion. The presence of this condition will affect the duration and distance necessary for the full shock to detonation process to be completed.

An E-Gun assembly, composed of a high voltage capacitive discharge unit coupled to an exploding foil, was used to generate planar shocks in the HMX. Specifics of the E-Gun used in this work may be found in [7]. The E-Gun generates a thin pulse shock boundary condition imparted into an explosive sample. For each flyer thickness, a threshold study was conducted using 25 samples. The data presented here are from experiments conducted using 3.8 mm square bridges. Flyer thicknesses that ranged from 31 µm to 203 µm of Parylene-C or a polyimide material were tested. The 3.8 mm square bridge results in an area with an effective diameter of approximately 4.3 mm. Kleinhanß et al. [11] studied ignition of PBXN-5, which is 95% HMX and 5% Viton-A, at the same density studied here and reported a critical ignition velocity as a function of spot size for thick flyers (250 µm). Their results imply the critical velocity for PBXN-5 stabilizes around impact diameters of 4 mm. This suggests the ignition behavior has become essentially one dimensional at that scale. Consequently, we expect the pure HMX materials studied here have similar one dimensional ignition characteristics. However, this has not been confirmed and it is recognized that a significant change in ignition behavior due to bed structure may affect conclusions.

To reduce variability of the input shock conditions to the explosive, chips from a single processed wafer of chips were used for each experimental series. A flight distance of approximately 900 µm was chosen for all flyer thicknesses. This distance helped to mitigate high voltage breakdown as well as allowed the flyer to approach a near terminal velocity. Shorter flight distances may have resulted in ambiguity in ignition behavior due to contributions of the high pressure bridge materials preventing sufficient relief of pressure post impact. That condition would begin to invalidate a simplified planar impact analysis of the ignition data. Given the above, the stand-off condition was set at 90-95% of the terminal velocity of the flyer plate. Some positive push was still desirable such that flyer shape was not becoming overly dynamic due to hydrodynamic instabilities.

Once the ignition data are collected, they were fitted to hyperbolic functions of an exponential form, which is shown in equation 2. This expression defines the relationship between the inert shock’s power flux, $\Pi$, and energy fluence, $E$, as reported in equations 3 and 4 that are present with the unreacted explosive. The trend line resulting from equation 2 represents conditions where the shock present within the explosive equals the Critical Ignition Condition. The original form of a hyperbolic initiation threshold function proposed by James [12] included two fitted constants where the form in equation 2 relies upon three. Additionally, $\Sigma [Up^2/2]$ was replaced by $\Pi$ in our relationship as defined below. The third term $E_a$ controls how rapidly the function transitions from an energy fluence limited condition to a power flux limited condition at the knee of the curve. The exponential form was chosen
based upon the implications of the underlying chemically reactive nature of the system that drives the heat release required to enable a successful ignition event. The various flyer thicknesses allow for the determination of different points on the hyperbolic ignition trend lines for a given bridge size. This, in turn, allows for the fitting of the constants ($\Pi_c$, $E_c$ and $E_a$) in the below equations.

$$\Pi = \Pi_c \cdot \exp \left( -\frac{E_a}{E_c - E} \right)$$  \hspace{1cm} (2)

$$E = P \cdot U_p \cdot \tau$$  \hspace{1cm} (3)

$$\Pi = P \cdot U_p$$  \hspace{1cm} (4)

Similar hyperbolic power-energy ignition criteria have been experimentally observed for hotwire and stab ignited devices and reported by Cooper [13]. Cooper's [13] use of Power vs. Energy plots did influence our selection of the above flux and fluence terms as well as personal communications [14]. In the above equations, $P$ and $U_p$ are the pressure and particle velocity developed within the HMX pellets. Those values are calculated, using a Mie-Grüneisen for the unreacted equation of states, by way of the impedance matching technique and using the E-Gun flyer velocity at the Critical Ignition Condition. Tau, $\tau$, is the duration of the shock pulse in the explosive. The flyer velocities were determined using a photonic Doppler velocimetry system.

Figure 5 reports the experimental conditions that were measured for the various flyer thicknesses and materials that resulted in a 50% probability of ignition for the Class III and V HMX pellets. Additionally, the trend lines that were fitted using equation 2 are plotted. As with previously studied HMX based materials, the exponential ignition functions are able to fit the measured data well [7]. The exponential form has also been used to fit ignition data for HNS [15] and TATB [16] with similarly good results. $\Pi_c$ and $E_c$ are the asymptotic conditions that are quantified using the fitted form of equation 2. $\Pi_c$ and $E_c$ were calculated to be 0.35 GW/cm$^2$ and 0.018 kJ/cm$^2$ for the Class III and 0.25 GW/cm$^2$ and 0.006 kJ/cm$^2$ for the Class V material.

5. Discussion and conclusions

The results shown in figure 5 and the associated parameters fitted to equation 2 suggest that there is a larger shift in $E_c$ relative to $\Pi_c$ for the two HMX materials studied. The fitted parameters indicate that $\Pi_c$ varies by 40% where $E_c$ varied by 200% for the data collected thus far using the Class V material as the reference condition. To further assess this result, we fitted the E-Gun data reported by Honodel et al. [16] to equation 2 and determined that $\Pi_c$ varied as much as 50% where $E_c$ varied as much as 130%. The types of TATB studied by Honodel et al. included ultrafine, superfine, fine, standard and production. $\Pi_c$ represents a shock condition within the explosive below which an initiation process may not be achieved and is energetic material specific. $E_c$ is surely also defined by the energetic material as well but seems to be a continuum level parameter that is more strongly varying with bed microstructure. Meaning, with TATB and HMX we have found that $E_c$ varies more significantly with
changes in primary powder particle morphology and more importantly with pressed bed microstructures. Moreover, we have found that $E_c$ is reduced when finer grained materials are utilized and the microstructures are more homogeneous over the length scale of the thin-pulse shock. An alternate means to globally quantified microstructural changes is by assessing the percent difference between the interfacial areas, as defined in table 1. The Class III contains 47% less interface area in the pre-shocked bed relative to the Class V material. Currently, no strong conclusions may be drawn due to the limited number of microstructures assessed thus far. Ongoing work includes additional materials such as fined grained fluid energy milled HMX so that we may assess effects of further homogenization of the microstructure.

With the above results in mind, a simplistic picture of the ignition process can be constructed. Figure 6 is an illustration that depicts a shock with a finite spatial width and amplitude entering two different microstructures of the same material and density. When considering a slower change in $\Pi_c$ as a function of microstructure, perhaps if both microstructures have sufficient quantities of critical ignition features $\Pi_c$ is most strongly affected by material. This would be due to those critical energy localization sites having sufficient time to coalesce given $\Pi_c$ is identified in a thick pulse ignition regime. For the limiting cases where $\Pi$ becomes large and the shock thicknesses becomes small (i.e. $E\rightarrow E_c$), microstructures with fewer of those critical energy localization sites must sustain $\Pi$ ($\Pi=P\cdot U_p$) for longer periods of time (i.e. larger $E=P\cdot U_p\cdot \tau$ values) to allow reaction sites to coalesce.

When considering critical scales, several may be quantified given the data generated during this work. The temporal and spatial length scales of the shocks ranged from $10\rightarrow 90$ ns and $57\rightarrow 410$ µm respectively for the HMX ignition studies. When considering a strong shock condition where $\Pi=1.4$ GW/cm$^2$ ($P=11$ GPa), the corresponding pulse spatial and temporal characteristics in the energetic material is calculated to be 65 µm and 13 ns for Class III and 24 µm and 5 ns for Class V for a Critical Ignition Condition. When considering a simplification of the 1-D thermal diffusion equation, $\frac{\partial T}{\partial t} = \alpha \cdot \frac{\partial^2 T}{\partial x^2}$, as estimated by $\delta x = \sqrt{\alpha \cdot \delta t}$ where $\alpha = \kappa / \rho \cdot C_p$ we may roughly estimate conduction length scales. The symbols are defined as follows: $\alpha$, thermal diffusivity, $\rho$, density, $C_p$, the specific heat at constant pressure and $\kappa$, thermal conductivity. Using thermal properties reported in [17], the thermal diffusion length may be calculated to be 42 nm and 25 nm for
the Class III and V materials respectively. This indicates that thermal activation of the bed via conduction will be localized to the ignition sites during the ignition pulse time scale presuming those sites are limited to the particle-to-particle boundaries. To qualitatively illustrate this, figure 7 plots the thermal conduction zones activated due to energy localizations at surfaces of the crystals. The Class V material is clearly more homogenous relative to the Class III material which has very large regions that may be thought of as cold spots assuming primary energy localizations sites are at grain boundaries. Stating another way, the thermal diffusion length is small compared to the distances between voids in the pre compacted bed. A point to remember is that figure 7 is the static condition prior to any shock loading so this visualization is qualitative in nature and essentially further illustrates variations in bed microstructure. Inclusions of hydrodynamic flow leading to pore collapse within the beds would essentially thicken these zones during the ignition event. Highly resolved simulations are needed to further enhance our understanding of how the different microstructures studied here may be leading to the ignition results measured experimentally.

In summary, we have reported on diverse experimental methods that quantified microstructures of pressed explosive beds and the ignition behavior of those beds for two HMX materials. Initial results indicate using a modified James criterion to assess effects of microstructural changes on continuum level ignition behavior may be viable. Future work will continue to assess these methods and to couple them to simulation efforts to further our understanding of ignition and growth phenomena.

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