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Abstract. The formation of hot spots is critical to the shock wave initiation of high explosive crystals. Hot spots are formed, for example, when micron-sized pores contained within the crystals are collapsed under shock wave loading. In this work, a numerical model is used to simulate pore collapse and chemical reactions in shock-loaded β-HMX crystal. The model accounts for (i) anisotropic, time-dependent mechanical responses of the crystalline phase, (ii) crystal melting due to localized deformation, and (iii) decomposition reactions that are driven by the temperature field. For a baseline set of model parameters, the simulations predict a modest extent of reaction over a nanosecond time scale. However, relatively small increases to the assumed viscosity of the liquid phase lead to significant increases in reactivity, due to intensified dissipation in shear banding regions.

Introduction

The shock wave initiation of high explosive (HE) materials is known to be controlled by localized regions of elevated temperature, i.e., hot spots [1, 2]. The hot spots are generated, for example, by interaction of the shock wave with material defects. Microscopic pores contained within HE crystals (or among aggregates of crystals) have long been considered as sources for the hot spots needed to trigger rapid chemical reactions under shock wave loading. Therefore, descriptions of shock wave ignition are typically linked to pore closure. However, a fundamental understanding of the ignition process is still lacking, as precise localization mechanisms, microstructure dependencies, and ignition time scales are largely unknown.

To improve our understanding of shock wave initiation, there is a need to resolve the dissipative processes that give rise to hot spots in HE crystal and subsequent chemical responses in those regions. Given the difficulty of accessing relevant time and length scales by experimental methods, we have pursued a computational approach. In this regard, a numerical model has been developed to simulate the shock initiation of porous β-HMX crystal. The model is unique in that it accounts for (i) the crystal mechanics, i.e., anisotropic thermoelastic-viscoplastic responses of the crystalline phase, and (ii) decomposition reactions that are driven by the local temperature. The model is used to study the collapse of a single intragranular pore in a crystal that is shock-loaded up to about 10 GPa. The reactivity of the sample is quantified over a post-collapse simulation time of a few nanoseconds (a time scale that is short, but relevant to the early stages of ignition under these conditions). A small parametric study is then undertaken to assess the model sensitivity to initial crystal orientation and the viscosity of molten HMX.

Material model

The most stable phase of HMX at standard pressure and temperature is the β phase. The β phase exhibits monoclinic crystal symmetry and can be represented in either of two equivalent space groups, $P2_1/n$ or $P2_1/c$, with two molecules per unit cell [3]. In the following, we describe a material model that has been developed to address the initiation of β-HMX crystal by shock wave loading. The material model integrates descriptions of the crystal mechanics, melting response, and decomposition chemistry. In this work, all crystal quantities are referenced to the $P2_1/c$ space group.

Let us begin by considering the decomposition chemistry. A number of multi-step reaction pathways have been proposed for the thermal initiation of β-HMX by slow heating processes [4–6]. However, the reaction path that is followed under shock wave loading, which involves high pressures and short time scales, is largely unknown. Given this uncertainty, we have adopted a single-step (global) reaction. The reaction addresses the decomposition of both β- and liquid-phase HMX, i.e.,

$$\begin{matrix}\text{HMX, } \beta\text{+liq} \\ (C_4H_8N_8O_8)\end{matrix} \longrightarrow \begin{matrix}\text{Product gas } (4\,CO+ \\ 4\,H_2+4\,N_2+2\,O_2)\end{matrix}$$

In this scheme, the chemical species to be tracked are HMX (β+liquid) and product gas. The reaction rate is modeled as first-order with respect to the HMX species and the Arrhenius kinetic parameters of Henson et al. [6] are utilized, i.e., an activation energy of E_a = 149 kJ/mol and a frequency factor of k_0 = 5.6×10^{12} s^{-1}. Although the single-step reaction is a simplification of the chemistry, it is sufficient to describe a wide range of experimentally-measured ignition times, including observations relevant to the shock ignition of β-HMX crystal [6]. Future efforts may consider both multi-step reactions and final products that contain water vapor instead of free oxygen.

With the reaction path and kinetics in hand, the various components of the the material model may now be formulated. The thermoelastic-viscoplastic responses of the β phase are handled using a crystal model that was developed in previous work [7]. The crystal model makes use of a Murnaghan equation-of-state (EOS) and a dislocation density based strength law. In this framework, plastic deformation of the crystalline phase occurs by the motion of dislocations on specific slip systems. Selected properties of the β phase (given at standard temperature and pressure) are given in Table 1. To allow for crystal melting, a compression-dependent melt energy curve is defined. As the material progresses through the melting phase transformation, a mixture rule is used to compute the deviatoric responses of the solid/liquid mixture. Here, the liquid phase is modeled as a viscous Newtonian fluid. The liquid viscosity is taken to be constant and equal to the value computed from atomistic simulations performed at 800 K and 1 atm, i.e., 5.5 cP [8]. The reference density and EOS of the liquid phase are taken to be identical to that of the β phase. This is assumed purely for expediency and it is recognized that refined treatments of the liquid phase would improve the model. The heat capacities of the β and liquid phases (again, assumed equivalent) are formulated as functions of temperature to improve the accuracy of computed temperature fields in the simulations. Further discussion of the material properties needed to simulate the shock wave ignition of HMX is available in the literature [9].

The decomposition chemistry is handled by the thermochemical code, Cheetah [10]. The material model interrogates the Cheetah code (i) to evolve the species concentrations based on the prescribed reaction kinetics and the thermodynamic state, and (ii) to compute the pressure and temperature of a multi-phase material point (β+liquid+gas) based on its density, internal energy, and composition. The conversion of β+liquid HMX to product gas involves an exothermic heat release of –4198 J/g, which is taken into account.

Numerical simulation of pore collapse

The numerical simulation of pore collapse in shock-loaded HE materials has been considered in previous computational efforts. For example, continuum mechanics based models have been constructed to study aggregates of HMX grains under dynamic loading [11–13] and the shock-induced closure of a single pore contained within HMX [7, 14] and TATB [15]. The progress of the current modeling framework is the inclusion of the crystal mechanics and decomposition chemistry.

Table 1. Selected properties of the β phase, given at standard pressure and temperature.

Property		β-HMX
Mass density – ρ_0	g/cm^3	1.904
Molar mass – M	g/mol	296.156
Bulk modulus – K_0	GPa	15.588
$n = (\partial K/\partial p)_0$	–	6.6
Volumetric CTE – α_0	1/K	0
Heat capacity – c_{p0}	J/g K	1.0
Melt temperature – T_{m0}	K	550

To simulate shock wave propagation, a numerical model was constructed using the multi-physics finite element code, ALE3D. The computational domain was rendered by inserting a single micron-sized pore near the center of a rectangular slab of β-HMX crystal. The pore is cylindrical in shape and filled with ambient air. To reduce the computational cost and complexity of these calculations, a 2D plane strain problem was considered. Although full 3D calculations are certainly desirable, we believe such calculations are premature at this stage of model development.

A shock wave is generated by prescribing the axial component of velocity on the left-hand surface of the crystal slab. The prescribed material velocity rises instantaneously, similar to conditions imposed at the impact surface in a plate impact experiment. The top and bottom surfaces of the crystal sample are periodic and the right-hand surface is restrained by a rigid frictionless wall. The initial dislocation density field of the crystal is not uniform, but rather randomly distributed in space to provide a more realistic description of the microstructure on the computational mesh (cf. Ref. [7]).

There is a large parameter space that can be studied with respect to modeling intragranular pore collapse. We have conducted a study by constructing a reference case and then perturbing that reference case to investigate various effects. In previous work [16], we reported on the sensitivity of the calculations to stress wave amplitude. In the following, we consider the effects of initial crystal orientation and the viscosity of molten HMX.

Simulation results

Reference case

The reference case involves a pore diameter of 1 μm, a velocity boundary condition of 1 km/s (which generates a plateau stress of 9.4 GPa), and a crystal orientation that is obtained as follows: the normal vector of the $(\bar{1}\bar{1}1)$ plane is aligned with the shock direction (x-axis); the crystal is then rotated about the shock direction until the $[1\bar{1}0]$ direction forms an angle of θ with the y-axis. To allow for comparison with previous work [7], the angle of rotation was selected as $\theta = -38.8°$. The reference case simulations are locally adiabatic (i.e., there is no heat conduction among the material points).

The reference case was considered in our previous work [16]. Under shock wave loading, the interaction of the wave with the pore leads to the jetting of liquid-HMX into the pore space and the growth of shear bands away from the pore collapse region. This shear banding behavior is illustrated in Fig. 1. The shear bands are a result of localized deformation in regions that tend to follow the orientation of specific crystallographic planes (e.g., the (011) and $(\bar{1}02)$ planes, as shown in Fig. 1). The dissipated work in these shear banding regions is sufficient to melt the material contained within the bands. Thus, the shear bands may be viewed as melt cracks.

In the pore collapse region (near the center of Fig. 1), a hot spot temperature of about 5000 K is present. This hot spot has been generated by mechanical work and exothermic heat release due to chemical reaction. In the reference case, the only region that undergoes reaction is the pore collapse region, as the shear bands do not reach high enough temperatures.

The reactivity of the sample is quantified by the relative mass of products, ξ, which is defined as the total mass of product phase (summed over the full sample) divided by the pore mass, i.e., the reference mass of crystal that would fit inside the initial pore. When considering the shock initiation of porous HE systems, a commonly used ignition criterion is $\xi \geq 1$. The product curve for the reference case (9.4 GPa) is plotted in Fig. 2, along with product curves simulated at lower and higher stress wave amplitudes [16]. Here, and in the remainder of this article, times are given relative to the arrival of the

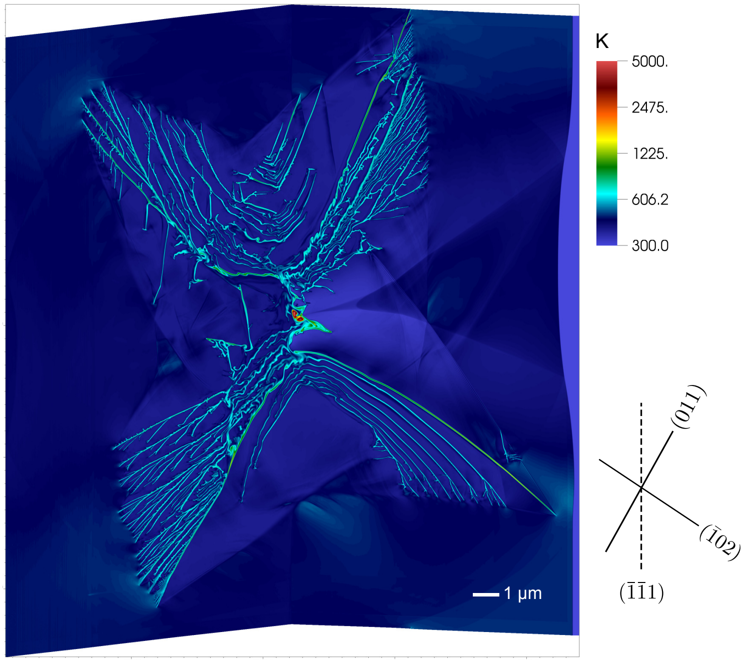


Fig. 1. The simulated temperature field for the reference case (temperatures plotted on a logarithmic scale). The shock wave direction is from left to right. This snapshot was taken at a time of 2.6 ns after the shock wave arrives at the pore. The narrow bands of elevated temperature are shear bands that have grown out of the pore collapse region.

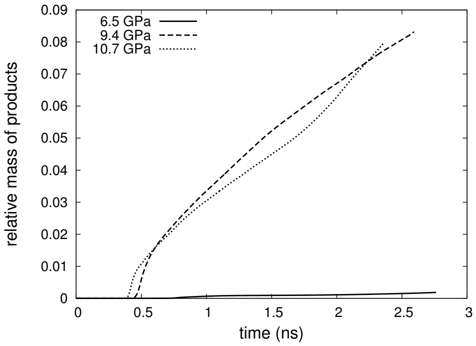


Fig. 2. Product curves for the reference case (9.4 GPa) and crystal samples that were simulated at lower and higher stress wave amplitudes.

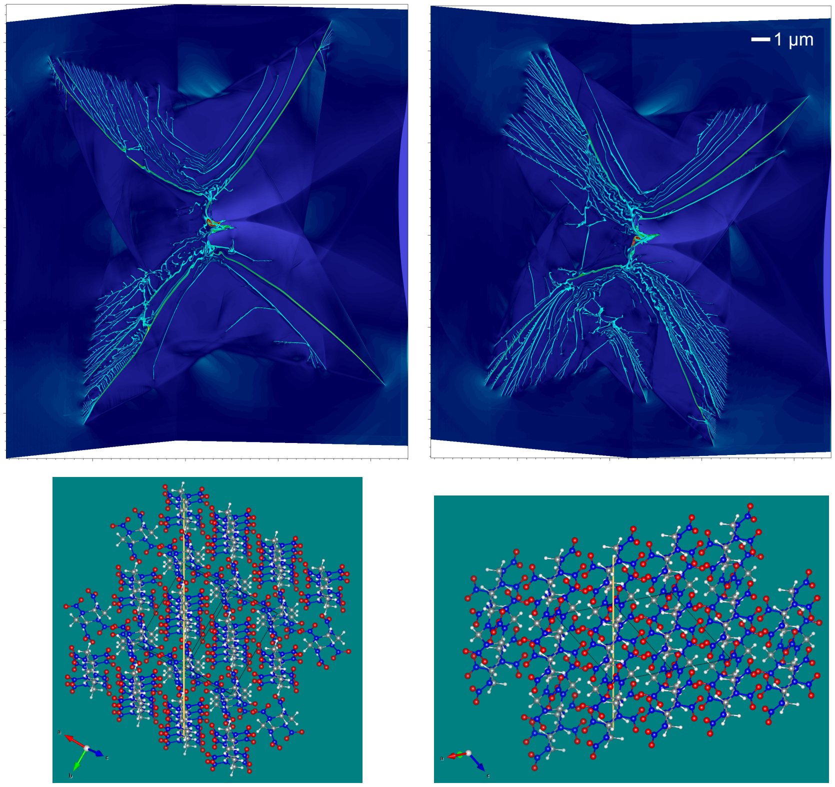
shock front at the left-hand-side of the pore.

Effects of crystal orientation

The sensitivity of the pore collapse model to crystal orientation was investigated by varying the angle of twist about the shock axis, θ. All other aspects of the reference case remained the same. Although the shock wave direction is still normal to the $(\bar{1}\bar{1}1)$ plane, the cylindrical pore axis is now re-oriented with respect to the crystal lattice. In addition to the reference case ($\theta = -38.8°$), twist angles of 0° and 90° were considered.

The temperature field for each of the new crystal orientations is plotted in Fig. 3. These fields may be compared to the temperature field for the reference case in Fig. 1. As shown in Fig. 3, the initial crystal orientation has some effect on the shear band patterning. This is because the shear bands tend to grow along the crystallographic planes that are subjected to the largest shear stresses (oriented about 45° away from the shock direction).

Although the computed temperature fields reveal some subtle differences (e.g., the 0°-case exhibits less crack branching and fewer closely spaced melt cracks when compared to the other orientations), the overall localization behavior does not appear to



θ = 0° θ = 90°

Fig. 3. The simulated shear band patterning is somewhat sensitive to the initial crystal orientation. The images in the bottom row depict the orientation of the crystal lattice for shock loading normal to the $(\bar{1}\bar{1}1)$ plane (indicated by the vertical plane in the figure) and twist angles of 0° and 90°. The corresponding temperature fields are plotted above. The temperature scale is the same as that given in Fig. 1.

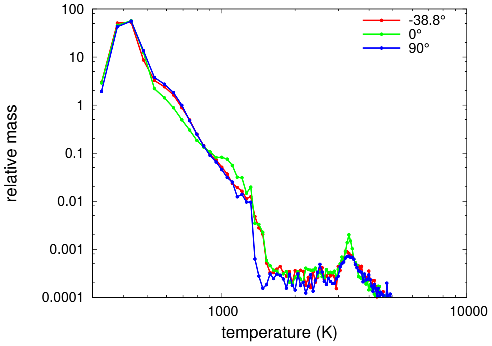


Fig. 4. Temperature histograms computed for various twist angles about the shock direction. The midpoints of the bins are plotted as closed symbols.

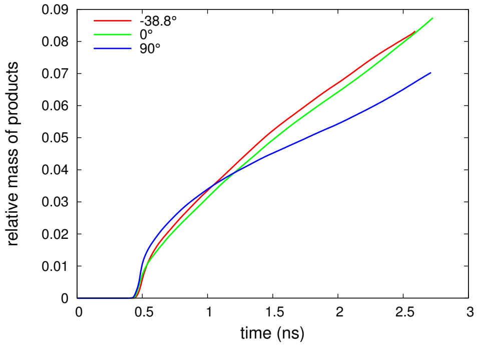


Fig. 5. Product curves for the various orientations illustrate that the simulated reactivity is relatively insensitive to twist angle when loading normal to $(\bar{1}\bar{1}1)$.

exhibit a strong dependence on crystal orientation. This is confirmed by the sample temperature histograms plotted in Fig. 4, which show similar temperature distributions among each of the orientations. These histograms were constructed by binning the mass of a sample according to temperature and normalizing by the pore mass. As such, the temperature histograms convey the relative mass of HMX that is found within a given temperature range. The high-temperature tail of the histogram ($>$ 2000 K) corresponds to regions that are partially or fully reacted. As shown in Fig. 5, the product curves for each of the orientations indicate that the reactivity of these samples is more-or-less the same on this time scale.

Effects of liquid viscosity

As mentioned earlier, the pore collapse simulations predict the formation of shear bands that are filled with liquid-HMX. We now consider the sensitivity of the model to the viscosity of the liquid phase. The viscosity of liquid-HMX has been computed in atomistic simulations that were performed at ambient pressure and temperatures ranging from 550 K (initial melting) to 800 K [8]. It was shown that the liquid viscosity conforms to the following relation: $\eta = \eta_0 \exp(T_a/T)$, where η_0 = 3.1×10^{-4} cP and T_a = 7800 K. In the reference case, a viscosity of 5.5 cP was utilized, which corresponds to a liquid temperature of about 800 K. The liquid viscosity is now increased to 22.0 cP, which corresponds to a liquid temperature of about 700 K. All other aspects of the reference case remain unchanged.

When the viscosity of the liquid phase is increased, the shock-loaded crystal samples exhibit higher reactivity in the pore collapse region and the shear bands. This is illustrated by the product curves given in Fig. 6. The initial trajectory of the product curve is controlled by reactions that occur in the fluidized pore collapse region (near the center of the sample). As shown in Fig. 6, the case with higher viscosity is more reactive over the first 2 ns of compression due to higher temperatures around the collapsed pore. At about 2 ns, there is a significant increase in the reaction rate. This increased rate of product formation is due to the occurrence of reactions in a few of the shear bands. In this case, the dissipated work renders some shear bands hot enough to react on a nanosecond time scale. Thus, the model is quite sensitive to the viscosity of the liquid phase.

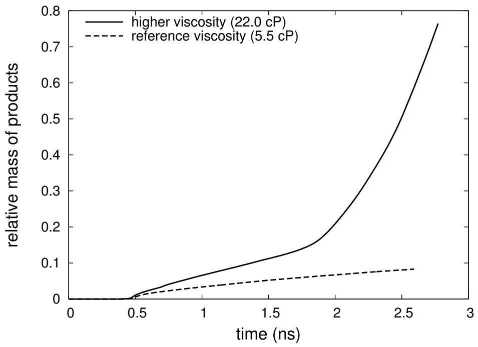


Fig. 6. Product curves for the reference case and the case with higher liquid viscosity. The rather sharp increase in reaction rate for the higher viscosity case corresponds to the onset of reactions in shear banding regions of the sample.

Conclusions

A numerical model has been used to study the shock wave initiation of porous β-HMX crystal. The model calculations, which are situated at the length scale of individual HE grains, focus on resolving hot spots generated by the collapse of intragranular pores and the attendant chemical reactions in those regions.

To obtain a baseline set of results for pore collapse in β-HMX crystal, a reference case was considered. The reference case involved a 1-μm diameter pore, shock loading normal to $(\bar{1}\bar{1}1)$, and a peak stress of 9.4 GPa. The reference case yielded a modest extent of reaction ($\xi \sim 0.1$) for a post collapse simulation time of a few nanoseconds. These calculation also revealed the importance of shear localization as a deformation mode of the defective crystal. The shear bands, which a filled with molten HMX, tend to propagate along crystal planes that are well-oriented for slip.

Simulations were then performed to assess the sensitivity of the model to (i) initial crystal orientation and (ii) the viscosity of the liquid-HMX phase. For loading normal to $(\bar{1}\bar{1}1)$, the simulated reactivity was relatively insensitive to changes in twist angle about the shock direction. It remains to be seen if this result holds for shocks propagated normal to other crystal planes. On the other hand, the model predictions of reactivity are quite sensitive to the viscosity of the liquid phase. When the liquid viscosity is increased from 5.5 cP to 22.0 cP, the overall reactivity increases rather sharply due to the occurrence of decomposition reactions in the shear bands. Shock wave ignition is nearly achieved for the sample with higher viscosity, as $\xi \sim 0.8$ on this time scale.

In consideration of these results, future modeling work should seek to develop more accurate treatments of the liquid phase EOS and viscosity. A relatively straight-forward extension of the current model would be to incorporate the aforementioned temperature-dependent viscosity [8] in the fluid constitutive model. Data on the pressure dependence of the liquid viscosity are also wanted, as these simulations involve pressures on the order of 10 GPa. Finally, techniques for extending the shock simulation time beyond a few nanoseconds are needed, at which point heat transfer away from the hot spots should be addressed.

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