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Unreacted Equation of State Development and Multiphase Modeling of Dynamic Compaction of Low Density Hexanitrostilbene (HNS) Pressings

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Abstract. Compaction waves in porous energetic materials have been shown to induce reaction under impact loading. In the past, simple two-state burn models such as the Arrhenius Burn model have been developed to predict slapper initiation in Hexanitrostilbene (HNS) pellets; however, a more sophisticated, fundamental approach is needed to predict the shock response during impact loading, especially in pellets that have been shown to have strong density gradients. The intergranular stress measures the resistance to bed compaction or the removal of void space due to particle packing and rearrangement. A constitutive model for the intergranular stress is needed for closure in the Baer-Nunziato (BN) multiphase mixture theory for reactive energetic materials. The intergranular stress was obtained from both quasi-static compaction experiments and from dynamic compaction experiments. Additionally, historical data and more recently acquired data for porous pellets compacted to high densities under shock loading were used for model assessment. Predicted particle velocity profiles under dynamic compaction were generally in good agreement with the experimental data. Hence, a multiphase model of HNS has been developed to extend current predictive capability.

Introduction

Hexanitrostilbene (HNS) is a thermally stable, secondary granular, high explosive that has been synthesized in the US for nearly 50 years.[1] HNS is often used in slapper detonator designs, but it is also used in a variety of aerospace applications (e.g. boosters), in linear shaped charge designs (e.g. wellbore perforating guns), and numerous US Department of Defense and Department of Energy applications.[2] A number of grades of HNS are available—HNS-I, HNS-II, HNS-FP, HNS-IV, and HNS-UF.[3] Each HNS polymorph is processed to optimize unique performance criteria; for slapper designs, neat HNS powders are pressed into pellets.

Anomalous performance behavior has been reported for HNS, where threshold energies for initiation were found to be inconsistent with expected trends in powder morphology.[3] For example, an increase in specific surface area did not necessarily lead to a decrease in explosive sensitivity. Schwartz[4] evaluated slapper detonator performance using three different HNS grades and demonstrated that shock initiation depends strongly upon particle morphology. Such research presents an open question regarding the link between particle morphology and explosive performance.

Modeling Approaches

Fundamentally, shock initiation is a multiscale phenomenon, beginning at atomistic scales and propagating to continuum length and time scales, as demonstrated by the research of Baer.[5] A novel mesoscale modeling technique was developed here at Sandia National Laboratories, where three-dimensional nanotomography was used to obtain realistic morphological geometry of high-density HNS-FP pressings and shock initiation from 30-micron slappers was simulated with the SNL Eulerian, finite volume, multidimensional, multimaterial shock physics code, CTH.[6,7] Such an approach is needed to unravel anomalous HNS performance measurements, and it holds promise for contributing to state-of-the-art multiscale modeling approaches; however, these mesoscale simulations are computationally intensive, given the significant computational resources required to resolve individual pores over the length scales required to model shock to detonation transition (SDT).

A complementary, less computationally expensive alternative approach to explicitly modeling the explosive heterogeneity at the mesoscale, which could include the energetic material (EM) and its binder (if present), is implicitly modeling the energetic material, such as with reactive burn models or multiphase models. Reactive burn models are phenomenological and they predict the progress of an extent of reaction variable, which tracks the history of the EM from unburned to fully reacted, based upon a fit of the model to Pop-plot data from wedge tests. A simple reactive burn model suitable for slapper initiation of HNS pellets is the Arrhenius Reactive Burn (ARB) model. This is a two-state, temperature-dependent (a pressure-dependent term is also included in CTH[8]) model based upon Arrhenius kinetics that was originally developed for homogeneous explosives, but can also be applied to very fine-grained solids, single crystals, and some non-explosive materials (e.g. molecular liquids or polymers). It is suitable for inputs from multiple shocks, ramp waves, and shocks with short pulse durations. If pressure dependence is ignored, the model is fit to Pop-plot data by adjusting two kinetic parameters, the frequency factor and the activation temperature. With only two adjustable parameters, it is not possible to accurately represent enough relevant physics to capture the wide body of initiation data available for HNS slapper detonators. Reactive, multiphase mixture models have been developed to characterize complex combustion phenomena in ball propellants and packed EM beds.

The Baer-Nunziato (BN) reactive multiphase model was developed according to the non-equilibrium theory of chemically reacting, multiphase mixtures to model thermal and shock initiation processes in porous, granular explosives.[9,10] The model considers two phases—the granular reactant phase and the gaseous detonation products. Conservation equations for mass, momentum, and energy are solved for each phase, and constitutive relationships are used for closure of the terms governing the mass, interphase force, and energy transfer between phases. Each phase is allowed to have independent thermodynamic and kinematic states, such as velocity, pressure, temperature, volume, etc. The BN model has been used to predict DDT phenomena in EMs under a variety of loading conditions. In particular, it was used to predict reaction induced by compaction waves from low-velocity impact of porous HMX packed beds.[11] Fitting this model to predict initiation in granular reactive materials requires a variety of relevant validation experiments and it can take multiple years adequately develop a multiphase combustion model that replicates experimental data. In this paper, the BN model was fit to dynamic compaction HNS experiments where the low-level shock impact was insufficient to initiate detonation.

Intergranular Stress Modeling

It is often desirable to design HNS pellets for slapper detonators to have a high surface area and low initiation threshold.[3] Optimal design of these slapper detonators requires detailed modeling of the compaction process. The granular bed is formed by pressing neat HNS granules (without binder), which form a matrix of irregularly shaped, brittle molecular crystals, which could fracture under high compressive stresses and bond at the crystalline contact points. Although the strength of these pressed beds is small, e.g. for 25-mg HNS pellets a yield strength of 0.14 GPa was reported,[12] at low input stress, strength is important.

The intergranular stress, β is a measure of the compressive stress in the grains due to the intergranular contact forces. The intergranular stress can also be considered as the resistance due to bed compaction. The resistance between grains is friction dominated; hence compaction, the removal of void space due to particle packing and rearrangement is rate dependent. Concomitantly, the intergranular stress represents the porous Hugoniot of the unreacted material (analogous to the Hermann P-α model), and it will be dependent upon initial particle size, morphology, temperature, strain rate and loading.[13] In the BN model,[10] the rate-dependent compaction is modeled by an evolution equation for solid volume fraction ϕ_s,

$$\frac{d\phi_s}{dt} = \frac{\phi_s(1-\phi_s)}{\mu_c}(p_s - \beta) \tag{1}$$

where β is only a function of ϕ_s, and the expression has been simplified for non-reactive problems. According to Eqn. (1), the time rate of change of ϕ_s following the motion of the solid is balanced by the compaction source term representing the instantaneous force balance between the solid pressure p_s and β, where μ_c is the compaction viscosity. For non-reactive problems, the gas pressure and the interphase mass transport terms can be neglected, and the problem can be considered as a single-phase solid, granular pressed bed. The intergranular stress relationship is given by,

$$\beta = \tau(\phi_s - \phi_{s0})^m \left[\frac{1-\phi_{s0}}{1-\phi_s}\right]^n \ln\left[\frac{1-\phi_{s0}}{1-\phi_s}\right] \tag{2}$$

where the coefficients are determined by fitting β to experimental data. This relationship was developed to fit HMX quasistatic compaction data.[14]

Intergranular Stress Measurements

Intergranular stress measurements are needed for closure in the BN multiphase model. Given the paucity of high strain rate compaction data for porous samples, quasistatic data are often applied for dynamic compaction processes, despite considerable differences in strain rate.[15] To fill a needed gap in HNS compaction data, quasistatic intergranular stress measurements were made using a unique pressing apparatus, as described by Cooper et al.[16] This reference includes the development of the experimental apparatus and its use for CL-20 powders. Herein, results are presented for the same apparatus, but with HNS-FP powders. For slow, quasistatic loading, mechanical equilibrium can be assumed. The intergranular stress in the porous bed is measured by the ratio of the average axial compressive force per unit radial cross-sectional area

$$\beta = \frac{F_a + F_t}{2A\phi_s} \tag{3}$$

where F_a is the applied force, F_t the transmitted force, and A the cross-sectional area.[14] To account for compression, the change in density with pressure, the crystalline density of the HNS-FP powder is evaluated with the relationship for a Birch-Murnaghan solid,[17] as given below

$$P = \frac{K_{T_0}}{N}\left[\left(\frac{\rho_s}{\rho_{s0}}\right)^N - 1\right] \tag{3}$$

where ρ_s is the crystalline density and ρ_{s0} is the initial crystalline density. The solid volume fraction is evaluated with the following expression

$$\phi_s = \frac{\rho}{\rho_s} \tag{4}$$

where ρ is the pellet density.

The fit provided in Eqn. (3) by Kipp et al.[17] was determined by fitting the relationship to isothermal compression data from HNS-I, HNS-II, and HNS-FP. Beyond 0.6 GPa, the hydrostatic compaction curves collapse.[18] Crystalline data obtained by mercury porosimetry were also reported, but this technique has been shown to yield inaccurate porosity measurements due to the inability of the mercury to fully invade the pore space, even under high pressures.[19] Moreover, high density HNS-FP pressings have predominantly isolated porosity.[20] Another isothermal relationship for HNS was provided by Sheffield et al.[21] This relationship, along with the other relationships by Kipp et al. and Setchell et al. are plotted in Figure 1. To date, the crystalline equation of state of HNS has not been reliable measured, but it has only been estimated or fit to other porous data.

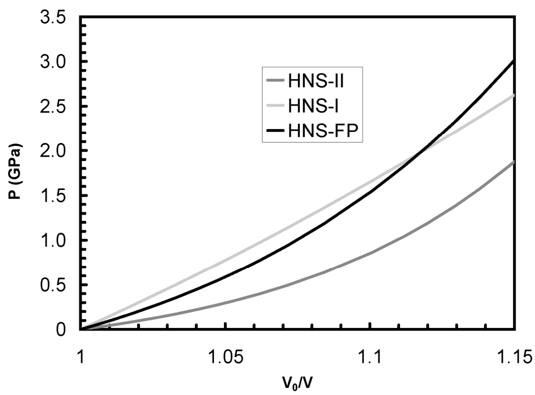

Fig. 1: Hydrostatic compressibility for crystalline HNS.[17,18,21]

A shock Hugoniot for the crystalline solid was estimated by fitting a linear u_s-U_p relationship to the gas-gun data shown in Fig. 2. The data reported by Sheffield et al.[21] were conducted on the Sandia light gas gun, where one X-cut quartz gauge was mounted on the projectile to record impact stress and another gauge was affixed to the rear of the target to record transmitted wave profiles. This setup produced redundant Hugoniot data, and the experimental uncertainty was reported to within 6%. Goveas et al.[22] reported planar impact experiments using a single stage gas gun. Pressed pellets of HNS-UF were instrumented with miniature Manganin stress gauges in a configuration designed to measure the shock loading response to high impact stresses. Shock Hugoniot data were recorded to 5.7 GPa. The good agreement between the estimated unreacted crystalline Hugoniot to the data suggests that the full compaction data from the two grades of HNS is largely independent of initial particle morphology, as evidenced by Goveas et al.[22]

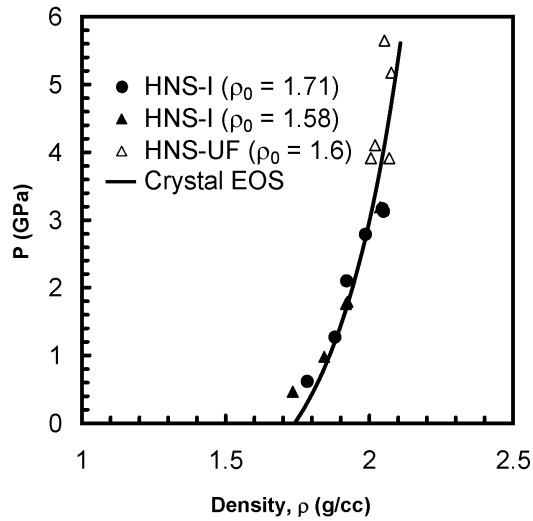

Fig. 2: Curve fit of crystalline shock Hugoniot to HNS-1 data from Sheffield et al.[21] and HNS-UF from Goveas et al.[22]

Quasistatic intergranular stress measurements on HNS-FP at slightly different free-pour packing fractions also indicate a response to loading that is independent of particle size, as shown in Fig. 3. Moreover, this observation can also be noted for intergranular stress computed from dynamic compaction data from HNS-I and HNS-II.[21] Quasistatic intergranular stress measurements for the HMX[14] have similar profiles, i.e. distinct linear regions as shown on semi-logarithmic plots, as those reported herein for HNS, which is also a nitramine explosive, although the HMX particle sizes are substantially larger than the fine-particle HNS material. Beyond a 40% TMD, the HNS curves coalesce, suggesting that widespread fracture occurs early and that the particle beds of each sample are similar. Hence, fracture in these materials produce similarly sized particles. To model dynamic compaction, intergranular stress measurements are needed and are obtained from the impact experiments reported by Sheffield et al., as previously noted.

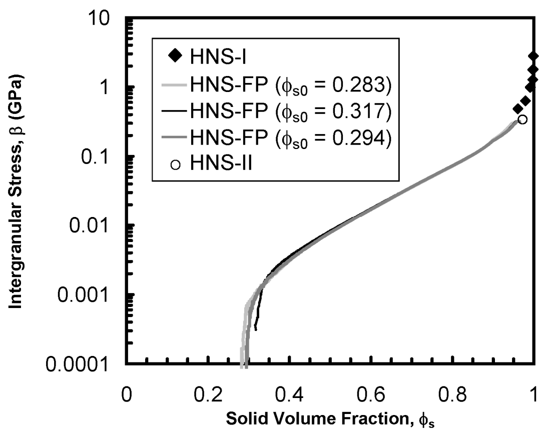

Fig. 3: Quasistatic and Dynamic Intergranular stress data.[21]

High strain rate intergranular stress measurements are fit with the model provided by Eqn. (2). This relationship is plotted in Fig. 4 and it has good agreement with the published data. The fitting coefficients are provided in the figure.

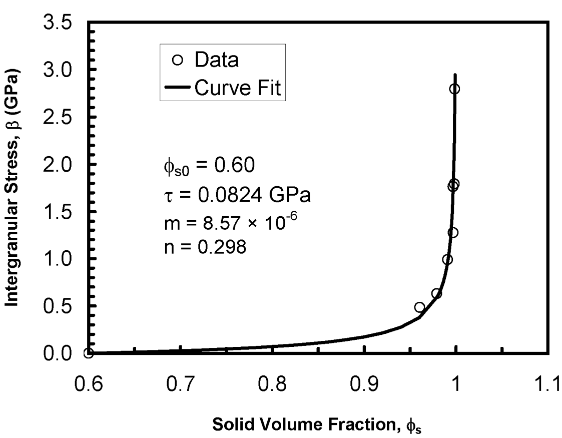

Fig. 4. Intergranular stress with Eqn. (2) and fitting coefficients.

Computational Results

In this section, the multiphase model is used to analyze low-velocity impact experiments conducted by Cooper.[23] HNS-FP powders were pressed to an initial density of approximately 70 %. To obtain direct Hugoniot measurements, the impact surface was unconfined and exposed. The pressed pellets elastically relaxed to a new density. As tested pellet densities were measured as 62.1 ± 2.3 %. Details of the experimental setup are provided by Cooper [16].

Thermophysical and material property data used in the multiphase modeling are listed in Table 1. Using these parameters and the ones listed for the intergranular stress relationship (e.g. Fig. 2), generally good comparisons between the model and the experiments were made.

Table 1. Equation of state and thermophysical property data for HNS

Variable (cgs units)	Value
d_p (μm)	2.7
ϕ_{s0}	0.60
ρ_{s0} (g/cm^3)	1.74
α_s (cm^2/s)	1.24×10^{-3}
k_s (erg/cm s K)	2.09×10^{4}
c_v (erg/g K)	8.88×10^{6}
μ_c (g/cm s)	33.3
$\Gamma_s \rho_s$ (g/cm^3)	2.83
s	2.4
C_0 (cm/s)	2.50×10^{5}

The computational results and the experimental velocity measurements are provided, parameterized by the flyer velocity u_f, in Figs. 5 and 6. The porous pellets do not transmit sharp shocks, instead, dispersion of the compaction waves is observed at the shock front. This has been observed in low-density pressings of HMX[24] and sugar[25] under weak shock loading. The presence of heterogeneity from grains, grain boundaries, pores, etc. adds structure to the compaction wave and tends to smear and spread the waves. In the multiphase model, the compaction viscosity, which controls the rate of volume fraction evolution towards equilibrium, was increased from 33.3 to 100 g/cm-s for the lowest impact shot at u_f = 0.1895 km/s. As evidenced in Fig. 5, more dispersion at the shock front occurs at lower impact velocities. As shown in Fig. 6, the duration of the ramp decreases with increasing impact velocity, which demonstrates the rate dependence of the compaction process. At the largest impact velocity, u_f = 0.8508 km/s, the model predicts the correct unreacted Hugoniot state; however, the compaction waves induce reaction in the material at later times not presented in the figure. Additional measurements are needed to understand the compressive wave phenomenology contributing to combustion. Such experiments are reported by Baer and Nunziato,[9] for example.

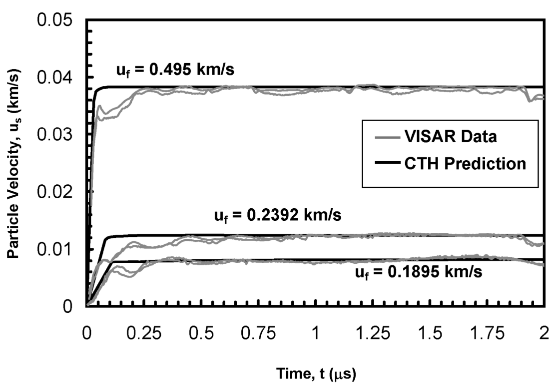

Fig. 5. Comparison of BN model to low-impact gas gun experiments for flyer velocities from 0.1895 to 0.495 km/s.

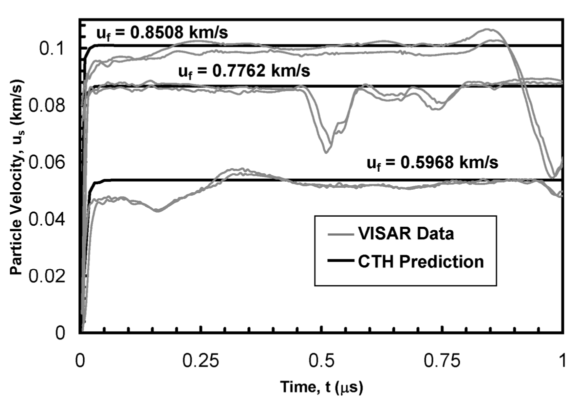

Fig. 6. Comparison of BN model to low-impact gas gun experiments for flyer velocities from 0.5968 to 0.8508 km/s.

Conclusions and Recommendations

To support multiphase model development for predicting the shock response of low-density HNS pressings, new quasistatic and dynamic compaction data were presented. This work adds to the limited body of literature available on low-density pressings of energetic materials. Such data were recently acquired for CL-20[16]. Furthermore, a Hugoniot curve for crystalline HNS was fit to historical and relatively recent data. With this new data, a BN model provided good agreement with the measurements.

Copious amounts of shock initiation data are available for HNS, but new data are needed for single crystals, such as pop-plot data and isothermal compression, to support novel equation of state development and new modeling approaches. Although the dynamic compaction data were sufficiently fit by the BN multiphase model, more measurements are required to provide data needed to fit the model to reactive wave experiments. This would provide an opportunity for a more fundamental understanding of HNS phenomenology and slapper detonator performance.

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