

Shock Induced Phase Transition of HMX Considering Initial Temperature effects

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1 Abstract

The purpose of this paper is to develop the crystal plasticity constitutive model to investigate the role of shock induced solid-solid phase transformation on the deformation mechanisms of HMX single crystal, which accounts for nonlinear elasticity, crystalline plasticity and temperature dependent phase transition (β -to- δ phase transition). In this work, the thermal-mechanical-chemical responses of HMX under shock loading with different initial temperatures have been investigated using finite element software ABAQUS. The temperature and phase transition fraction increase with the rising initial temperature. The comparisons between considering the temperature effects and a lack of the temperature effects are also discussed in this paper. The averaged stress and temperature profiles of HMX along wave propagation direction are higher when considering the temperature effects. The responses along different crystal orientation under shock compression are also discussed in this paper. The shock response of β -to- δ phase transition is orientation dependent.

2 Introduction

HMX is one of the most important solid-state energetic materials. There exist four solid phase polymorphs for HMX, denoted as α , β , γ , δ . The most stable form at room temperature is the monoclinic β phase [1], and the δ phase is considered to be stable at high temperature. The δ phase is created from the β phase by heating between 432-438K or above 463K and at ambient pressure [2]. The stability of the polymorphs is as follows: $\beta > \alpha > \gamma > \delta$ [3], which is also the order of density.

The phase transition investigations of polymorphs have been a focus for the safety of the energetic materials in recent years, and abundant researches have been done about the β -to- δ phase transition of HMX. The HMX chemical decomposition includes four reaction processes and the first is the β -to- δ phase transition [4]. Phase changes in energetic materials are important because of the resulting change in density. Explosive performance metrics (detonation pressure and detonation velocity) are related to the density [5]. It was speculated that the observed sensitivity increase of the δ -phase is due to a significant

lattice expansion and the associated density decrease from 1.90 for β to 1.76 g/cm³ for δ , accompanying the β -to- δ phase transition [6], which results in an appearance of cracks, large amount of hot spots in the material, and the fast growth of reaction during shock compression [7]. Yao Long and Jun Chen [8] developed a phonon-electron free energy model to study the thermodynamic properties and phase transitions of HMX, and they obtained the bulk modulus, thermal expansion coefficient, Hugoniot curve, and phase transition curve over a wide range of temperature and pressure.

Most of the previous studies have investigated the shock induced phase transition of HMX by experiments and molecular dynamics. In this work, we develop a mesoscale constitutive model by considering temperature dependent phase transition to analyze the response of shock induced phase transition in HMX.

3 Model

In this section, a brief outline is presented of the thermal mechanical constitutive model for HMX crystals. The constitutive model for HMX crystals used in this study follows that developed by Wu and Huang [9] to interpret the planar impact experiments on HMX single crystals by Dick et al. [10] and Wang and Wu and Huang [11] to simulate the thermal-mechanical response of impacted granular and polymer-bonded explosives. The development extends earlier works on crystal plasticity to cases where the modeling of response at high pressure is considered. Henson et al [12] constructed a model to describe the β -to- δ phase transition of HMX crystals under high pressure and temperature.

Based on multiplicative decomposition and polar decomposition, the deformation gradient \mathbf{F} can be indicated as,

$$\mathbf{F} = \mathbf{F}^e \cdot \mathbf{F}^p = \mathbf{R}^e \cdot \mathbf{U}^e \cdot \mathbf{F}^p \quad (1)$$

where \mathbf{F}^e denotes elastic deformation, \mathbf{F}^p denotes plastic deformation. \mathbf{F}^e can be decomposed into \mathbf{R}^e and \mathbf{U}^e , which respectively denotes thermoelastic crystalline lattice right stretch tensor and crystalline lattice rotation tensor.

The plastic deformation of a crystal is assumed only to be due to dislocation motion on crystalline slip systems,

$$\mathbf{L}^p = \dot{\mathbf{F}}^p \mathbf{F}^{p-1} = \sum_{\alpha=1}^n (\bar{\mathbf{s}}^{(\alpha)} \otimes \bar{\mathbf{m}}^{(\alpha)}) \dot{\gamma}^{(\alpha)} \quad (2)$$

where $\bar{\mathbf{s}}^{(\alpha)}$ is the slip direction of a particular slip system α and $\bar{\mathbf{m}}^{(\alpha)}$ is the slip plane normal, $\dot{\gamma}^{(\alpha)}$ denotes the shear strain rate of slip system α .

The Orowan equation is in the description of shear strain rate for rate-dependent crystal plasticity,

$$\dot{\gamma}^{(\alpha)} = \rho_m^{(\alpha)} b^{(\alpha)} \bar{v}^{(\alpha)} \quad (3)$$

where $b^{(\alpha)}$ is the Burgers vector, $\rho_m^{(\alpha)}$ is mobile dislocation density, $\bar{v}^{(\alpha)}$ is the average dislocation velocity of slip system α . The dislocation velocity is assumed to be related to the resolved shear stress $\tau^{(\alpha)}$,

$$\bar{v}^{(\alpha)} = v_0^{(\alpha)} \exp \left[\frac{-s_d}{(\tau^{(\alpha)} - \tau_0)} \right] \quad (4)$$

where $v_0^{(\alpha)}$ is shear wave velocity, s_d is drag stress, τ_0 is the threshold shear stress for dislocation motion. The dislocation velocities are limited to be less than the shear wave velocity at the corresponding shear slip plane.

Both nucleation of dislocation and growth of existing loops are considered in the slip kinetics,

$$\dot{\rho}_m^{(\alpha)} = M\dot{\gamma}^{(\alpha)} \exp(-H\bar{\gamma}/\tau^{(\alpha)}) + A(\tau - \tau_c)\dot{t} \quad (5)$$

where $\bar{\gamma} = \sum_{\alpha=1}^n \int_0^t |\dot{\gamma}^{(\alpha)}| dt$ denotes the total cumulative shear strain on each slip system; τ_c is the threshold shear stress for dislocation nucleation; M , H and A are material constants.

The nonlinear thermo-elasticity model includes anisotropic elastic and thermal effects. The complete expression for the rate-form constitutive equation is,

$$\dot{\sigma}^L = \bar{\mathbf{C}} : \bar{\mathbf{D}}^e + \frac{1}{2} \bar{\boldsymbol{\varepsilon}}^e : \frac{\partial \bar{\mathbf{C}}}{\partial \bar{\boldsymbol{\varepsilon}}^e} : \bar{\mathbf{D}}^e - \rho T \boldsymbol{\Gamma} \dot{S} - \sum_{\alpha} (\mathbf{W}^{(\alpha)} \cdot \sigma^L - \sigma^L \cdot \mathbf{W}^{(\alpha)}) \quad (6)$$

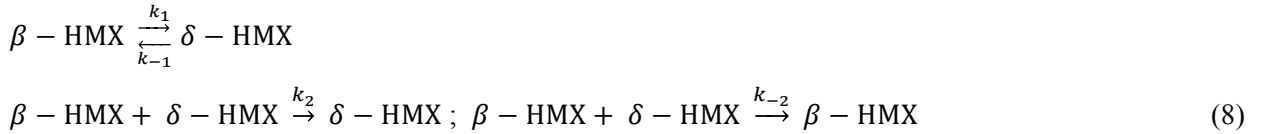
where $\bar{\mathbf{C}}$ is the pressure and temperature dependent second-order isentropic elasticity tensor, \mathbf{W} is the antisymmetric spin tensor, $\bar{\mathbf{D}}^e$ is the strain rate tensor, $\boldsymbol{\Gamma}$ is the anisotropic Grüneisen tensor and \dot{S} is the rate of increase of entropy.

To complete the thermo-dynamic description, the rate of temperature increase is given by,

$$\dot{T} = -T \boldsymbol{\Gamma} \mathbf{D}^e + \frac{T}{C_V} \dot{S} \quad (7)$$

where C_V is the specific heat at constant volume and a linearly increasing function of temperature $C_V = 667.7 + 0.88T$ ($J \cdot kg^{-1}/K^{-1}$).

The $\beta \rightarrow \delta$ phase transition in HMX single crystal occurs via nucleation and growth. Henson et al. [12] constructed a two state kinetic model of the system considering equilibrium terms first order in the β or δ mole fraction simulating nucleation, and second order in β and δ simulating growth. The four component processes, along with each labeled rate constant, are represented schematically below,



where k_1 , k_{-1} , k_2 , k_{-2} are four temperature and pressure dependent rate constants described by eight parameters. The rate constants are selected based on the free energy of an activated transition state from transition state theory,

$$k_i = \frac{k_B T}{h} Q_i \left[\frac{TS_i - (U_i + PV_i)}{RT} \right] \quad (9)$$

where k_B is Boltzman's constant, h is Plank's constant, U_i , S_i , V_i are the activation energy, entropy and volume of the activated state respectively, R is gas constant, Q_i is an equilibrium constant relating the concentrations of molecules in the activated transition state to those of the stable reagents.

The phase transition velocity v_{ph} can be obtained by Eq. (8) and Eq. (9), and the mole density of β -HMX single crystal $\beta_0 = 0.0064 \text{ mole/cm}^3$.

$$v_{ph} = \frac{\partial x}{\partial t} = \frac{\partial[\delta]/\beta_0}{\partial t} = k_1 + [\beta_0(k_2 - k_{-2}) - (k_1 + k_{-1})]x + \beta_0(k_{-2} - k_2)x^2 \quad (10)$$

4 Results and discussions

The proposed model has been implemented as a VUMAT in the ABAQUS/Explicit finite element software code [13]. VUMAT is a user subroutine which is used to define the mechanical constitutive

behavior of a material. HMX single crystal is constructed as $1\text{mm}\times 1\text{mm}\times 1\text{mm}$ 3D model as shown in Figure 1.

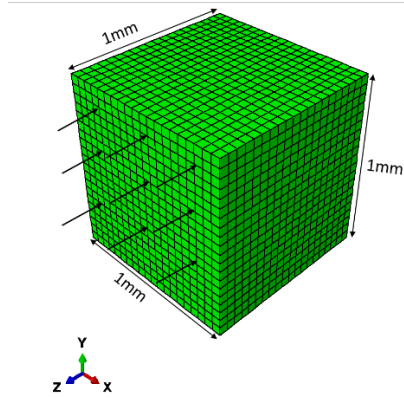


Figure 1. Finite element mesh for the single crystal cube with uniform pressure to the shock plane

The comparisons between considering initial temperature effects and a lack of initial temperature effects under shock loading 1GPa and initial temperature 300K in the averaged stress and temperature profiles of HMX along the wave propagation at 0.1 and 0.3 μs are obtained and plotted in Figure 2. When considering temperature effects, the averaged stress profile along wave propagation direction will be enhanced, as shown in Figure 2a. The temperature increase is caused by volumetric work and plastic work, and the phase transition latent heat will result in temperature decrease. From the Figure 2b, we can see the temperature profiles are higher when considering the temperature effects. The volumetric work plays a major role in temperature increase.

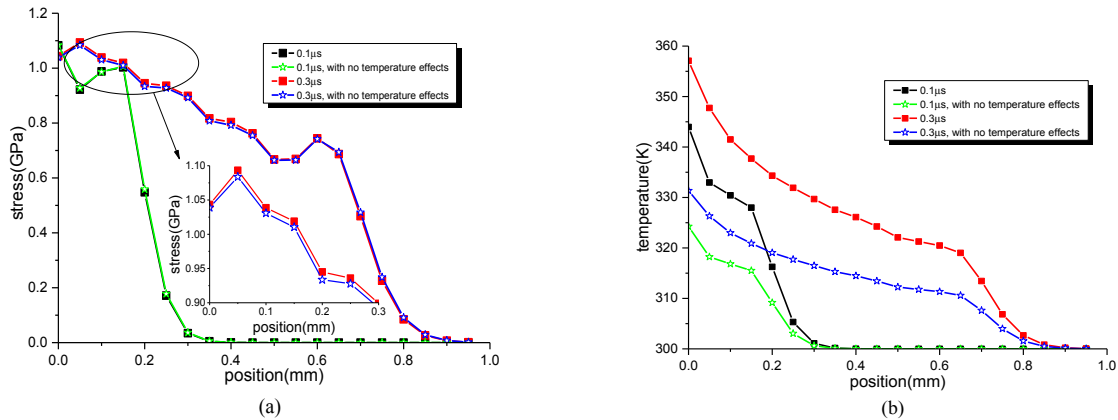


Figure 2. The comparisons between considering initial temperature effects and a lack of initial temperature effects in the averaged (a) stress and (b) temperature profiles of HMX along the wave propagation

The overall phase transition fraction of the sample, which means the fraction of δ -HMX, at different initial temperature from 300K to 425K under 1GPa shock loading is plotted in Figure 3a. The higher the initial temperature, the larger the phase transition fraction and velocity. Figure 3b shows the fraction of δ -HMX and temperature along the shock direction at an initial temperature of 375K. We can see that the temperature increases at 0.1 and 0.15 μs are apparently higher than 0.05 μs . The thermal expansion

coefficient of δ -HMX is smaller than β -HMX, and the volumetric strain is higher after the phase transition. Thus, the temperature increase caused by volumetric work is higher.

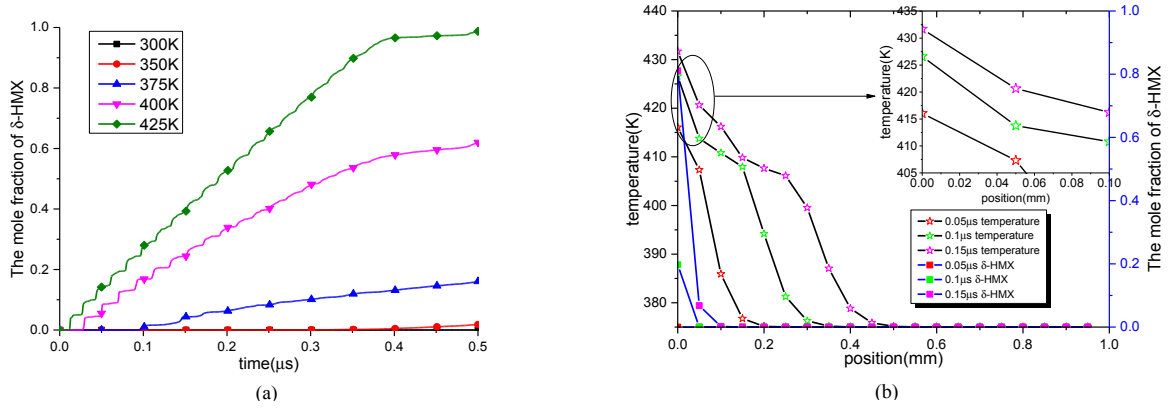


Figure 3. (a) The fraction of δ -HMX of the all HMX single crystal; (b) The fraction of δ -HMX and temperature along the shock direction at 375K initial temperature.

We also investigate the shock induced phase transition of HMX at different crystal orientations under 400K initial temperature and 1GPa shock loading which is shown in Figure 4. We observe that the phase transition of HMX single crystal is orientation dependent. When shock loading is along different direction, different slip systems will start, and it will result in different pressure and different temperature. As the phase transition fraction is strongly influenced by pressure and temperature, the phase transition is anisotropic. The phase transition fraction is the largest along (010) orientation and is the smallest along (100) orientation.

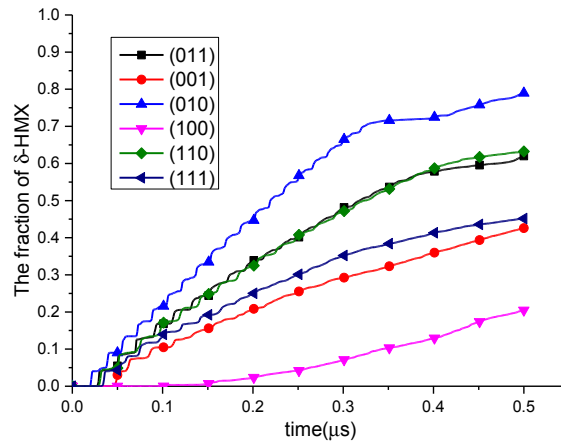


Figure 4. The fraction of δ -HMX along different direction

5 Conclusions

The thermal-mechanical-chemical responses of HMX under shock loading considering initial temperature effects have been investigated based on a crystal plasticity constitutive model that accounts for nonlinear

elasticity, crystalline plasticity and temperature dependent phase transition. The HMX single crystal is shocked by 1GPa under initial temperature from 300K to 425K to study the shock induced phase transition.

The stress, temperature and phase transition fraction profiles at different initial temperatures are compared. When considering initial temperature effects, the evolutions of stress and temperature profiles are quicker. The temperature and phase transition profiles will be enhanced with increasing initial temperature. Moreover, the phase transition of HMX is anisotropic. Consequently, the HMX is more sensitive when considering initial temperature effects.

In the future work, the developed mesoscale model of HMX should consider the chemical reactions and the effect of thermal damage so that it will provide better predictions of initiation of explosives.

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