A phase-field model for shock-induced α - γ phase transition of RDX

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Abstract

A thermodynamically consistent continuum phase-field model has been developed to investigate the role of shock-induced solid-solid phase transformation in the deformation mechanisms of molecular single crystals. The effects of microstructural evolution and phase transformation are distinguished and modeled within a crystal plasticity framework that is developed for single crystals at high strain rate. When applied to 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) single crystal, the model predicts α - γ phase transition within the experimentally observed range of shock stresses. Phase-field simulations suggest that the α - γ phase transition requires finite time to occur, where plasticity tends to delay the transition. Phase transformation is associated with stress relaxation, and increased temperature rise and associated shock-sensitivity. The shock response of α - γ phase transition is orientation dependent.

Keywords: phase transformation; high strain rate; shock loading; crystal plasticity; energetic material

1. Introduction

Shock compression of crystalline solids leads to intense deposition of elastic strain energy which produces sudden change in pressure and temperature (Duvall and Graham, 1977). Strain energy dissipation may occur through plastic deformation and/or polymorphic transformation which is diffusionless and displacive in nature (Meyers, 1994). While the anisotropic elastic-plastic response of shocked single crystals has been studied extensively (Becker, 2004; Winey and Gupta, 2006, 2010; Lukyanov, 2008; Barton et al., 2009; De et al., 2014; Lloyd et al., 2014), the modeling of the effects of shock-induced phase transformation on the deformation mechanisms of single crystal has received much less consideration. Vattré and Denoual (2016) proposed a phase-field formalism coupled with elastoplastic deformation for martensitic phase transition under high hydrostatic compression. Here, we present a thermodynamically consistent continuum phase-field model that accounts for the microstructural effects and physics of high strain rate to study the effects of shock-induced solid-solid phase transition on the deformation mechanism of single crystals. The proposed phase-field model is applied to investigate the shock-response of α - γ phase transition in 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) molecular single crystal.

RDX is known to exist as α , β , γ , δ , and ϵ polymorphs, with the α -phase being most stable under ambient conditions. Phase transformation studies on RDX using both the static compression (Dreger and Gupta, 2010) and shock wave compression (Patterson et al., 2007; Dang et al., 2010) experiments establish that RDX undergoes a α - γ phase transformation in the pressure range of 3.5-4.5GPa, regardless of crystal orientation

(Patterson et al., 2007) and temperature in the range of 295-460K (Dreger and Gupta, 2010). The transformation is reversible (Patterson et al., 2007) and accompanied by 3% reduction in the unit cell volume, and changes in the space group and molecular conformations (Davidson et al., 2008; Dreger et al., 2008). α -RDX has an orthorhombic structure of *Pbca* space group (Choi and Prince, 1972), whereas, γ -RDX is orthorhombic with *Pca*₂₁ space group (Davidson et al., 2008). An open question is the role of α - γ phase transition in the sensitivity of RDX.

Shock compression experiments on RDX display time-dependence of α - γ phase transition. The transition to γ -phase does not occur immediately above transition pressure (Patterson et al., 2007). Based on the stress history data for the shock loading on (111) plane of RDX, Patterson et al. (2007) conclude that the phase transition requires finite time to occur (~ 100 ns). This is significant as this is the same time scale on which shock initiation occurs in RDX (Dreger et al., 2008). Hence, it is imperative to model α - γ phase transformation in order to investigate its role in the shock sensitivity of RDX.

While anisotropic elastic-plastic response of both the α -RDX (Clayton and Becker, 2012; LaBarbera and Zikry, 2013; De et al., 2014) and the γ -RDX (Josyula et al., 2016) has been studied, continuum modeling of α - γ phase transition that accounts for crystal orientation, defect evolution, and high strain rate effects has not been undertaken.

Various continuum phase-field models have been developed to study the phase transformation in energetic materials. A configurational force balance (Gurtin, 1996) based phase evolution equation with chemical reaction is proposed to describe successive phase transformation in octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) from solid to liquid to gas (Ruderman et al., 2003). A thermodynamically consistent phase-field model is developed to study the β - δ phase transformation in HMX via stress induced intermediate interfacial melt below the melting temperature (Momeni and Levitas, 2015). Several other phase-field approaches have been developed to model martensitic transformation in context of plasticity theory (Hallberg et al., 2007; Kundin et al., 2011; Sadjadpour et al., 2015; Yeddu et al., 2016). For example, a phase-field model for martensitic transformation is developed to capture the interaction between phase transformation and dislocations at the nanoscale (Levitas and Javanbakht, 2015). A comprehensive review is presented in (Levitas and Javanbakht, 2015; Vattré and Denoual, 2016). For α - γ phase transition in RDX, transformational process such as kinetics of interface orientation, and evolution of microstructures in the interface region has not been very well understood.

In this paper, we present a thermodynamically consistent continuum phase-field model for the shock-induced solid-solid phase transition of single crystals. The phase-field evolution equation is derived using configurational force balance laws (Gurtin, 1996). The effects of microstructural evolution and phase transformation are modeled within a single crystal plasticity framework that is developed for high strain rate loading conditions (De et al., 2014). Various other rate-dependent crystal plasticity models based on kinetics of evolving dislocations have been developed for metals at high strain rate (Austin and McDowell, 2011; Krasnikov et al., 2011). The slip resistance model considered here incorporates microscopic mechanisms of dislocation motion and generation, defect annihilation and phonon drag, which are observed at high loading

rates (De et al., 2014). Nano-fracturing and internal cracking has not been reported for the single crystal of RDX shocked in the range of 3-5.5GPa, i.e. around the phase transition pressure of 3.5-4.5GPa (Patterson et al., 2007). Hence, fracture has not been considered in this model.

The thermomechanical response of shocked single crystal is obtained by solving the continuum momentum balance equation coupled with phase evolution equation. The thermodynamics of phase transformation is described using a Helmholtz free energy functional comprised of elastic potential energy and local interfacial energy based on the Cahn–Hilliard formalism (Cahn and Hilliard, 1958). The α - γ phase transition of RDX single crystal is studied for the impact loading on (100), (210), and (111) planes. These loading orientations have been analyzed extensively in previous experimental work on α - γ phase change of shocked RDX (Patterson et al., 2007; Dang et al., 2010).

The paper is organized as follows. The phase-field model along with crystal plasticity formulation for single crystals at high strain rate is presented in Section 2. The model parameters and the simulation results are discussed in Section 3, followed by conclusions in Section 4.

We follow notations that are standard in modern continuum mechanics (Gurtin, 1981). In particular, ∇ and $\nabla \cdot (\cdot)$ denotes the gradient and divergence with respect to material point $\mathbf{X}$, respectively. The time derivative of a field $\varphi(\mathbf{X}, t)$ is denoted by $\dot{\varphi}(\mathbf{X}, t)$, whereas, derivative of a scalar valued function $f(\cdot)$ is denoted as $f'(\cdot)$.

2. Phase-field model

A thermodynamically consistent continuum phase-field model has been developed for the shock-induced solid-solid phase transformation, without chemical decomposition, in molecular single crystals at high strain rate. The single crystal plasticity model developed for high strain rate loading (De et al., 2014) is extended to include phase transformation using a phase-field formulation. A state variable known as ‘order parameter’ is introduced to describe continuum measure of the degree of molecular order/disorder across the phase boundary. The non-conserved order parameter is associated with the molecular conformation and crystal structure. The secondary phase transformation has not been observed experimentally in the single crystal of RDX shocked below decomposition threshold (Patterson et al., 2007; Dreger, 2012). Hence, we do not consider secondary phase transformation in this model.

In the following Section 2.1 through 2.7, we present the kinematics of single crystal deformation with phase change, governing equations of the phase-field model, constitutive relations, temperature evolution equations, free energy functional that includes elastic potential and components associated with phase change, single crystal plasticity model, and finite element formulation, respectively.

2.1. Kinematics

Let $\mathbf{x} = \varphi(\mathbf{X}, t) : \Omega_0 \times \mathbb{R} \rightarrow \mathbb{R}^d$ with $d \in \{1, 2, 3\}$ be a nonlinear deformation map at time $t \in \mathbb{R}^+$ that maps material point $\mathbf{X}$ in the reference configuration $\Omega_0 \in \mathbb{R}^d$ at

temperature θ_0 to point $\mathbf{x}$ in the current configuration $\Omega \in \mathbb{R}^d$ at temperature θ through an intermediate stress-free configurations $\hat{\Omega} \in \mathbb{R}^d$, see Fig. 1. The current configuration is described by the deformation gradient tensor

$$\mathbf{F} = \partial\varphi(\mathbf{X}, t)/\partial\mathbf{X}; \det\mathbf{F} > 0. \quad (1)$$

$\mathbf{F}^p$ denotes the deformation gradient tensor related to plastic shear from the reference configuration Ω_0 to the unstressed configuration $\hat{\Omega}$. As the crystal deforms, the parent-phase (Phase-1) may transform to product-phase (Phase-2) with different crystal structure. This structural transformation is described by the transformation deformation gradient tensor $\mathbf{F}^t$. The current configuration is reached by lattice deformation and local rigid body rotation, which is contained in the elastic deformation gradient tensor $\mathbf{F}^e$. Hence, $\mathbf{F}$ is presumed to possess the multiplicative decomposition as

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^t \mathbf{F}^p, \det\mathbf{F}^e > 0, \det\mathbf{F}^t > 0, \det\mathbf{F}^p = 1, \quad (2)$$

where $\det\mathbf{F}^e$ and $\det\mathbf{F}^t$ is the measure of the volume change produced by elastic deformation and phase transformation, respectively. A similar three-term decomposition of $\mathbf{F}$ into elastic, transformational (e.g. twinning (Clayton, 2009, 2010), and martensitic transformation (Kouznetsova and Geers, 2008; Levitas and Javanbakht, 2015; Vattré and Denoual, 2016)), and plastic part has been proposed elsewhere.

Fig. 1. Kinematics of single crystal deformation with phase change.

We introduce a normalized order parameter $\phi: \Omega_0 \times (0, T) \rightarrow [0, 1]$ to account for this structural transformation, where $(0, T) \subset \mathbb{R}^+$ is a time interval, $\phi = 0$ and $\phi = 1$ denotes Phase-1 and -2, respectively, and $\phi \in (0, 1)$ at the interface boundary.

Let $\mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1}$ be the spatial velocity gradient tensor. Using Eq. (2), we obtain the following additive decomposition

$$\mathbf{L} = \dot{\mathbf{F}}^e \mathbf{F}^{e-1} + \mathbf{F}^e \dot{\mathbf{F}}^t \mathbf{F}^{t-1} \mathbf{F}^{e-1} + \mathbf{F}^* \hat{\mathbf{L}}^p \mathbf{F}^{*-1} \quad (3)$$

with $\mathbf{F}^* = \mathbf{F}^e \mathbf{F}^t$, where $\hat{\mathbf{L}}^p = \dot{\mathbf{F}}^p \mathbf{F}^{p-1}$ denotes the rate of plastic deformation relative to the intermediate configuration $\hat{\Omega}$.

The spatial velocity gradient of the plastic shear flow is expressed as

$$\dot{\mathbf{F}}^p \mathbf{F}^{p-1} = [1 - f(\phi)] \sum_{\alpha} \dot{\gamma}^{\alpha} \mathbf{s}_1^{\alpha} \otimes \mathbf{m}_1^{\alpha} + f(\phi) \sum_{\alpha} \dot{\gamma}^{\alpha} \mathbf{s}_2^{\alpha} \otimes \mathbf{m}_2^{\alpha}, \quad (4)$$

where $f: [0,1] \rightarrow [0,1]$ is a monotonically increasing function that satisfies $f(0)=0$, $f(1)=1$, and vanishing derivative condition at end points, i.e. $f'(0)=f'(1)=0$; $\dot{\gamma}^{\alpha}$ is the slip rate on slip system ' α ' in the pure phases (Phase- $i \in \{1,2\}$) with slip direction $\mathbf{s}_i^{\alpha}$ and slip plane normal $\mathbf{m}_i^{\alpha}$ in the reference configuration, which is mapped to the current configuration as $\mathbf{s}_i'^{\alpha} = \mathbf{F}^e \mathbf{s}_i^{\alpha}$ and $\mathbf{m}_i'^{\alpha} = \mathbf{F}^{e-T} \mathbf{m}_i^{\alpha}$, respectively (Fig. 1).

We assume a 2-3-4 polynomial as the monotonically increasing function (Levitas and Preston, 2002)

$$f(\phi) = a\phi^2 + 2(2-a)\phi^3 + (a-3)\phi^4, \quad 0 < a < 6, \quad (5)$$

which for parameter $a=3$ degenerates to a cubic polynomial that has been deemed appropriate for modeling flat interfaces (Clayton and Knap, 2011).

The transformation deformation gradient tensor for the diffusionless and displacive structural transformation can be described as

$$\mathbf{F}^t = \mathbf{I} + [f(\phi)](\mathbf{F}^{tr} - \mathbf{I}), \quad (6)$$

where the total transformation deformation gradient is given as $\mathbf{F}^{tr} = \mathbf{I} + \mathbf{s}_0 \otimes \mathbf{m}_0$ (Wayman, 1964; Nishiyama, 1978), where $\mathbf{m}_0$ is the habit plane unit normal and $\mathbf{s}_0$ is the shape deformation vector in the reference configuration, and $\mathbf{I}$ denotes the second order unit tensor.

The elastic deformation is characterized using Green-Lagrangian strain measure

$$\mathbf{E}^e = \frac{1}{2}(\mathbf{C}^e - \mathbf{I}), \quad \mathbf{C}^e = \mathbf{F}^{eT} \mathbf{F}^e, \quad (7)$$

where $\mathbf{C}^e$ defines the right Cauchy-Green deformation tensor.

The symmetric Piola-Kirchhoff type stress measure $\hat{\mathbf{S}}$ with respect to the intermediate configuration $\hat{\Omega}$ can be expressed as

$$\hat{\mathbf{S}} = \mathbf{F}^t \mathbf{F}^p \mathbf{S} \mathbf{F}^{pT} \mathbf{F}^{tT}; \quad \mathbf{P} = \mathbf{F}^e \hat{\mathbf{S}} \mathbf{F}^{t-T} \mathbf{F}^{p-T}; \quad \mathbf{P} = \mathbf{F} \mathbf{S}, \quad (8)$$

where $\mathbf{P}$ and $\mathbf{S}$ denotes first and second Piola-Kirchhoff stress tensor, respectively.

2.2. Balance laws

The governing equations to solve for the shock-induced phase transformation without chemical reaction include mass, momentum, and energy balance equations of continuum mechanics (Gurtin, 1981) coupled with configurational force balance equation (Gurtin,

1996) in conjunction with the dissipation inequality. Shock induces transient, localized, and excessive material deformation in an adiabatic process. Hence, the energy balance is formulated in the absence of heat transfer or internal energy source in the system. The balance laws in the local form can be written as the referential field equations as:

$$\text{Mass balance:} \quad \rho_0 = \rho \det \mathbf{F} = \rho J \quad (9)$$

$$\text{Balance of linear momentum:} \quad \nabla \cdot \mathbf{P} + \mathbf{b}^0 = \rho_0 \ddot{\mathbf{u}} \quad (10)$$

$$\text{Balance of angular momentum:} \quad \mathbf{F}\mathbf{P} = \mathbf{P}^T \mathbf{F}^T \quad (11)$$

$$\text{Microforce balance:} \quad \nabla \cdot \boldsymbol{\xi} + \pi + \gamma = 0 \quad (12)$$

$$\text{Energy balance:} \quad \rho_0 \dot{\psi} = \mathbf{P} : \dot{\mathbf{F}} + \boldsymbol{\xi} \cdot \nabla \dot{\phi} - \pi \dot{\phi} \quad (13)$$

$$\text{Dissipation inequality:} \quad \rho_0 \dot{\psi} + \rho_0 \eta \dot{\theta} - \mathbf{P} : \dot{\mathbf{F}} - \boldsymbol{\xi} \cdot \nabla \dot{\phi} + \pi \dot{\phi} \leq 0, \quad (14)$$

where ρ_0 is the reference density, ρ is density in motion, $\mathbf{b}^0$ is the reference body force, $\mathbf{u} = (\mathbf{x} - \mathbf{X}) \in U$ (here, U denotes the space of kinematically admissible displacements), $\boldsymbol{\xi}$ denotes the vector microstress, the scalar body forces π and γ represent, respectively, the internal and external microforce, ψ is the specific free energy, and η denotes specific entropy.

2.3. Constitutive relations

We begin with the dissipation inequality from Eq. (14), which can be rewritten using the multiplicative decomposition of deformation gradient tensor in Eq. (2) as

$$\begin{aligned} & \rho_0 \dot{\psi} + \rho_0 \eta \dot{\theta} - \mathbf{P} \mathbf{F}^{pT} \mathbf{F}^{iT} : \dot{\mathbf{F}}^e - \mathbf{F}^{eT} \mathbf{P} \mathbf{F}^{pT} : \left[\partial \mathbf{F}^t / \partial \phi \right] \dot{\phi} \\ & - \mathbf{F}^{iT} \mathbf{F}^{eT} \mathbf{P} : \dot{\mathbf{F}}^p - \boldsymbol{\xi} \cdot \nabla \dot{\phi} + \pi \dot{\phi} \leq 0 \end{aligned} \quad (15)$$

Let us assume a general form of free energy functional

$$\psi \equiv \hat{\psi}(\mathbf{F}^e, \theta, \phi, \nabla \phi, q_n) \quad (16)$$

for which the axiom of material objectivity requires $\psi(\mathbf{F}^e, \bullet) = \psi(\mathbf{Q}\mathbf{F}^e, \bullet)$ for any proper orthogonal tensor $\mathbf{Q}$. The set of internal variables ' q_n ' evolves with plastic loading.

The rate of change of free energy can be expressed as

$$\dot{\psi} = \frac{\partial \psi}{\partial \mathbf{F}^e} : \dot{\mathbf{F}}^e + \frac{\partial \psi}{\partial \theta} \dot{\theta} + \frac{\partial \psi}{\partial \phi} \dot{\phi} + \frac{\partial \psi}{\partial \nabla \phi} \cdot \nabla \dot{\phi} + \sum_k \frac{\partial \psi}{\partial q_k} \dot{q}_k. \quad (17)$$

Substituting Eq. (17) into the dissipation inequality in Eq. (15) yields

$$\begin{aligned}
& \left(\rho_0 \frac{\partial \psi}{\partial \mathbf{F}^e} - \mathbf{P} \mathbf{F}^{pT} \mathbf{F}^{tT} \right) : \dot{\mathbf{F}}^e + \rho_0 \left(\frac{\partial \psi}{\partial \theta} + \eta \right) \dot{\theta} + \left(\rho_0 \frac{\partial \psi}{\partial \nabla \phi} - \boldsymbol{\xi} \right) \cdot \nabla \dot{\phi} \\
& + \left(\rho_0 \frac{\partial \psi}{\partial \phi} - \mathbf{F}^{eT} \mathbf{P} \mathbf{F}^{pT} : \left[\partial \mathbf{F}^t / \partial \phi \right] + \pi \right) \dot{\phi} + \rho_0 \sum_k \frac{\partial \psi}{\partial q_k} \dot{q}_k - \mathbf{F}^{tT} \mathbf{F}^{eT} \mathbf{P} : \dot{\mathbf{F}}^p \leq 0
\end{aligned} \tag{18}$$

The above inequality (Eq. (18)) holds for all admissible deformation, temperature and phase-field, leading to the following restrictions on the stress tensor, entropy, and configurational stress

$$\mathbf{P} = \rho_0 \frac{\partial \psi}{\partial \mathbf{F}^e} \mathbf{F}^{t-T} \mathbf{F}^{p-T}, \tag{19}$$

$$\eta = -\frac{\partial \psi}{\partial \theta}, \tag{20}$$

$$\boldsymbol{\xi} = \rho_0 \frac{\partial \psi}{\partial \nabla \phi}. \tag{21}$$

The reduced dissipation inequality becomes

$$\left(\rho_0 \frac{\partial \psi}{\partial \phi} - \mathbf{F}^{eT} \mathbf{P} \mathbf{F}^{pT} : \left[\partial \mathbf{F}^t / \partial \phi \right] + \pi \right) \dot{\phi} + \rho_0 \sum_k \frac{\partial \psi}{\partial q_k} \dot{q}_k - \mathbf{F}^{tT} \mathbf{F}^{eT} \mathbf{P} : \dot{\mathbf{F}}^p \leq 0. \tag{22}$$

We require the phase change to be dissipative, hence,

$$-\beta \dot{\phi} = \rho_0 \frac{\partial \psi}{\partial \phi} - \mathbf{F}^{eT} \mathbf{P} \mathbf{F}^{pT} : \left[\partial \mathbf{F}^t / \partial \phi \right] + \pi, \tag{23}$$

where $\beta > 0$ is a kinetic coefficient. Using restriction on $\boldsymbol{\xi}$ and π from Eq. (21) and (23) in conjunction with microforce balance equation (Eq. (11)) leads to the phase-field evolution equation

$$\beta \dot{\phi} = \nabla \cdot \left(\rho_0 \frac{\partial \psi}{\partial \nabla \phi} \right) - \rho_0 \frac{\partial \psi}{\partial \phi} + \mathbf{F}^{eT} \mathbf{P} \mathbf{F}^{pT} : \left[\partial \mathbf{F}^t / \partial \phi \right] + \gamma. \tag{24}$$

For the free energy of the form $\psi \equiv \hat{\psi}(\mathbf{F}^e(\mathbf{F}, \phi), \phi, \bullet)$, the second and third term in Eq. (24) can be viewed as $-\rho_0 \left(\frac{\partial \psi}{\partial \phi} \right)_{(\mathbf{F}, \bullet)} = -\rho_0 \left[\left(\frac{\partial \psi}{\partial \phi} \right)_{(\mathbf{F}^e, \bullet)} + \left(\frac{\partial \psi}{\partial \mathbf{F}^e} \right)_{(\phi, \bullet)} : \left(\frac{\partial \mathbf{F}^e}{\partial \phi} \right)_{(\mathbf{F}, \bullet)} \right]$. Hence, with this simplification and in the absence of external microforce, i.e. $\gamma = 0$, Eq. (24) can be written as $\beta \dot{\phi} = \nabla \cdot \left(\rho_0 \frac{\partial \psi}{\partial \nabla \phi} \right) - \rho_0 \left(\frac{\partial \psi}{\partial \phi} \right)_{(\mathbf{F}, \bullet)}$. Given a functional form of free energy with quadratic dependence on $\nabla \phi$, this equation reduces to a time dependent *Ginzburg-Landau equation* (Allen and Cahn, 1979).

2.4. Temperature evolution equation

Introducing Legendre transform of the internal energy, i.e. $\psi = e - \theta\eta$ into the energy balance Eq. (13) along with Eq. (17) for the rate of change of free energy, and constitutive equations (Eq. (19)-(21) and Eq. (23)) gives the following entropy evolution equation

$$\rho_0 \theta \dot{\eta} = \mathbf{F}^{iT} \mathbf{F}^{eT} \mathbf{P} : \dot{\mathbf{F}}^p + \beta \dot{\phi}^2 - \rho_0 \sum_k \frac{\partial \psi}{\partial q_k} \dot{q}_k. \quad (25)$$

Further, using Gibbs' relation, i.e. $\eta = -\partial\psi/\partial\theta$, the rate of change of entropy takes the following form

$$-\dot{\eta} = \frac{\partial^2 \psi}{\partial \theta \partial \mathbf{F}^e} : \dot{\mathbf{F}}^e + \frac{\partial^2 \psi}{\partial \theta^2} \dot{\theta} + \sum_k \frac{\partial^2 \psi}{\partial \theta \partial q_k} \dot{q}_k + \frac{\partial^2 \psi}{\partial \theta \partial \phi} \dot{\phi} + \frac{\partial^2 \psi}{\partial \theta \partial \nabla \phi} \cdot \nabla \dot{\phi}. \quad (26)$$

Using classical definition of the specific heat at constant deformation, i.e.

$$c_{\mathbf{F}^e} \equiv \theta \frac{\partial \eta}{\partial \theta} = -\theta \frac{\partial^2 \psi}{\partial \theta^2} \quad (27)$$

and Grüneisen tensor at constant temperature, i.e.

$$\mathbf{\Gamma} \equiv \frac{1}{c_{\mathbf{F}^e}} \mathbf{F}^{e-1} \frac{\partial \eta}{\partial \mathbf{F}^e} = -\frac{1}{c_{\mathbf{F}^e}} \mathbf{F}^{e-1} \frac{\partial^2 \psi}{\partial \theta \partial \mathbf{F}^e} \quad (28)$$

the entropy evolution Eq. (26) becomes

$$\dot{\eta} = c_{\mathbf{F}^e} \mathbf{F}^e \mathbf{\Gamma} : \dot{\mathbf{F}}^e + \frac{c_{\mathbf{F}^e}}{\theta} \dot{\theta} - \sum_k \frac{\partial^2 \psi}{\partial \theta \partial q_k} \dot{q}_k - \frac{\partial^2 \psi}{\partial \theta \partial \phi} \dot{\phi} - \frac{\partial^2 \psi}{\partial \theta \partial \nabla \phi} \cdot \nabla \dot{\phi}. \quad (29)$$

From Eqs (25) and (29), the temperature evolution equation can be derived as

$$\begin{aligned} \rho_0 c_{\mathbf{F}^e} \dot{\theta} = & \mathbf{F}^{iT} \mathbf{F}^{eT} \mathbf{P} : \dot{\mathbf{F}}^p + \beta \dot{\phi}^2 - \rho_0 c_{\mathbf{F}^e} \theta \mathbf{F}^e \mathbf{\Gamma} : \dot{\mathbf{F}}^e \\ & - \sum_k \left(Q_k - \theta \frac{\partial Q_k}{\partial \theta} \right) \dot{q}_k + \rho_0 \theta \frac{\partial^2 \psi}{\partial \theta \partial \phi} \dot{\phi} + \rho_0 \theta \frac{\partial^2 \psi}{\partial \theta \partial \nabla \phi} \cdot \nabla \dot{\phi}, \end{aligned} \quad (30)$$

where $Q_n = \rho_0 \partial\psi/\partial q_n$ is the work conjugate to q_n . The first and third terms in the temperature evolution Eq. (30) contribute to plastic dissipation and thermoelastic heating, respectively.

Remark. An alternative form of Grüneisen tensor is $\mathbf{\Gamma} = \mathbf{C} : \boldsymbol{\beta} / \rho c_p$ (Wallace, 1972), where $\mathbf{C}$ is the fourth order elasticity tensor, $\boldsymbol{\beta}$ is the second order coefficient of thermal expansion tensor, and c_p denotes the specific heat capacity at constant pressure.

2.5. Helmholtz free energy

The Helmholtz free energy per unit reference volume is partitioned into elastic potential energy ψ_e and energy components associated with the phase change, i.e. phase

transition energy density ψ_ϕ and potential energy stored at the phase boundary $\psi_{\nabla\phi}$, such that $\rho_0\psi = \psi_e + \psi_\phi + \psi_{\nabla\phi}$. The local interfacial energy based on the Cahn–Hilliard formalism (Cahn and Hilliard, 1958) is given as

$$\psi_\phi = A\phi^2(\phi-1)^2 \quad (31)$$

$$\psi_{\nabla\phi} = \frac{1}{2}\kappa|\nabla\phi|^2; \quad \kappa > 0, \quad (32)$$

where $A>0$ represents the potential well depth for the double well potential with isolated zeros at $\phi=0,1$. In the isotropic approximation, the driving force A and the parameter κ in Eq. (32) are related to the interface surface energy Γ and the interface boundary thickness l via (Wheeler, 1999)

$$A = 12\frac{\Gamma}{l}, \quad \kappa = \frac{3}{2}\Gamma l. \quad (33)$$

We assume the following form of strain energy density

$$\psi_e = \frac{1}{2}\mathbf{E}^e : \mathbf{C}(\phi) : \mathbf{E}^e, \quad (34)$$

where the fourth-order elasticity tensor is defined as $\mathbf{C}(\phi) = \mathbf{C}(0) + [\mathbf{C}(1) - \mathbf{C}(0)]f(\phi)$.

An important part of the constitutive model for shocked material is the pressure-volume equation of state (EOS), which describes the volumetric response of the material. The EOS is incorporated in the constitutive equation (Eq. (19)) by separating the volumetric and deviatoric deformations.

Let us consider a kinematic split of the deformation $\mathbf{F}^* = \mathbf{F}^e \mathbf{F}^l$ into volumetric $J = \det \mathbf{F}^*$ and deviatoric (volume preserving) part as

$$\bar{\mathbf{F}}^* = J^{-1/3} \mathbf{F}^*, \quad \det \bar{\mathbf{F}}^* = 1, \quad \bar{\mathbf{C}}^* = J^{-2/3} \mathbf{C}^*, \quad (35)$$

where $J = J^e J^l$ such that $J^e = \det \mathbf{F}^e$ and $J^l = \det \mathbf{F}^l$ accounts for, respectively, the volume change produced by elastic deformation and dilatational transformation.

With the above kinematic split, we may rewrite the constitutive relation (Eq. (19)) for the symmetric Piola-Kirchhoff type stress as (Lubliner, 2008)

$$\hat{\mathbf{S}} \equiv \mathbf{F}^{*-1} \mathbf{P} \mathbf{F}^{*T} = -p J \mathbf{C}^{*-1} + J^{-2/3} \text{Dev} \left[2\rho_0 \partial\psi / \partial \bar{\mathbf{C}}^* \right], \quad (36)$$

where $p = \rho_0 \partial\psi / \partial J$ denotes the hydrostatic pressure, and ‘Dev’ denotes the Lagrangian deviator operator with $\text{Dev}[\cdot] = (\cdot) - \frac{1}{3}[\mathbf{C}^* : (\cdot)]\mathbf{C}^{*-1}$.

The volumetric (pressure) response, including the effects of transformation volume change on pressure, is described by a third-order Birch-Murnaghan equation of state (BMEOS) (Birch, 1947)

$$p = \frac{3K_0(\phi)}{2} \left[\left(\frac{V}{V_0} \right)^{-7/3} - \left(\frac{V}{V_0} \right)^{-5/3} \right] \left\{ 1 + \frac{3}{4} (K'_0(\phi) - 4) \left[\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right] \right\}, \quad (37)$$

where V/V_0 denotes volumetric change, $K_0(\phi)$ and $K'_0(\phi)$ are the bulk modulus and its pressure derivative with respect to pressure at 0Pa, respectively. Here, $K_0(\phi)$ and $K'_0(\phi)$ are defined the same way as the coefficients of the elasticity tensor. The BMEOS in Eq. (37) is deemed suitable for describing the volumetric response of RDX (Davidson et al., 2008; De et al., 2014). The deviatoric response of the shocked single crystal is represented by a fully anisotropic single crystal model, which is designed for high strain rate loading conditions (De et al., 2014).

2.6. Single crystal plasticity

The effects of microstructural evolution are accounted using a single crystal plasticity model. A major part of a crystal plasticity problem is to uniquely determine the plastic slip rate ' $\dot{\gamma}^\alpha$ ' that satisfy the plastic flow condition $f(\tau^\alpha, \tau_y^\alpha)$ on each slip system (Simo and Hughes, 1998; Nemat-Nasser and Hori, 1999) in respective phases as

$$f(\tau^\alpha, \tau_y^\alpha) = \begin{cases} = 0 & \text{if } \dot{\gamma}^\alpha \neq 0 \\ < 0 & \text{if } \dot{\gamma}^\alpha = 0 \\ > 0 & \text{inaccessible} \end{cases}, \quad (38)$$

where τ^α is the resolved shear stress, and τ_y^α is the slip resistance on the ' α ' slip plane. The resolved shear stress on any slip system ' α ' is computed as

$$\tau^\alpha = (\mathbf{C}^e \hat{\mathbf{S}}) : (\mathbf{s}_i^\alpha \otimes \mathbf{m}_i^\alpha), \quad i \in \{1, 2\}. \quad (39)$$

The constitutive behavior of the plastic slip is governed by the flow condition (Eq. (38)) along with an evolution equation for the slip resistance τ_y^α .

We have developed a slip resistance model that incorporates microscopic mechanisms of dislocation motion and generation, defect annihilation and phonon drag, which are observed at high loading rates. The rate sensitive power law hardening equation is given as (De et al., 2014)

$$\tau_y^\alpha = \frac{\mu(\phi)}{\mu_0(\phi)} \tau_0^\alpha \left\{ 1 + \left[1 + B(\bar{\gamma} + \gamma_0)^n \right] \left(\frac{|\dot{\gamma}^\alpha| + \dot{\gamma}_{off}}{\dot{\gamma}_0} \right)^m \exp(-\lambda \Delta Q) - \exp\left(-\frac{|\dot{\gamma}^\alpha|}{\dot{\gamma}_{p0}^\alpha}\right) \right\} \text{sgn}(\dot{\gamma}^\alpha), \quad (40)$$

where $\mu(\phi)$ and $\mu_0(\phi)$ are the current and reference elastic shear modulus, respectively, τ_0^α is the initial critical resolved shear stress, B is a drag coefficient, $\bar{\gamma} = \int_0^t \sum_\alpha |\dot{\gamma}^\alpha| dt$ is the total accumulated shear strain on all slip systems in respective phases; n , m , γ_0 , $\dot{\gamma}_{off}$,

and $\dot{\gamma}_0$ are other materials parameters, λ is a constant and ΔQ is the specific thermal energy increase from the initial state, $\dot{\gamma}_{p0}^\alpha$ represents an effective damping coefficient affecting dislocation glide. The parameter $\dot{\gamma}_{off}$ is introduced into the model to yield a meaningful finite strength to the material at zero slip activity.

2.7. Finite element formulation

The weak form of the governing equilibrium equations of elastodynamics in total Lagrangian approach (Bathe, 1995) may be stated as

$$\text{Find } \mathbf{u} = (\mathbf{x} - \mathbf{X}) \in H^1(\Omega_0 \times (0, T)) \text{ such that}$$

$$\int_{\Omega_0} \delta \mathbf{F}^T : \mathbf{P} d\Omega = \int_{\Omega_0} \delta \mathbf{u}^T \mathbf{b}^0 d\Omega + \int_{\Gamma_t^0} \delta \mathbf{u}^T \bar{\mathbf{t}}^0 d\Gamma + \int_{\Omega_0} \delta \mathbf{u}^T \rho_0 \ddot{\mathbf{u}} d\Omega \quad (41)$$

satisfying boundary conditions

$$\mathbf{u} = \bar{\mathbf{u}} \text{ on } \Gamma_u^0 \times (0, T) \quad (42)$$

$$\mathbf{P}^T \mathbf{n}^0 = \bar{\mathbf{t}}^0 \text{ on } \Gamma_t^0 \times (0, T), \quad (43)$$

and initial conditions

$$\mathbf{u}(\mathbf{X}, 0) = {}^0\mathbf{u}(\mathbf{X}) \text{ on } \Omega_0 \quad (44)$$

$$\dot{\mathbf{u}}(\mathbf{X}, 0) = {}^0\dot{\mathbf{u}}(\mathbf{X}) \text{ on } \Omega_0, \quad (45)$$

where $\Omega_0 \in \mathbb{R}^d$; $d \in \{1, 2, 3\}$ is an open bounded domain with boundary $\Gamma^0 = \Gamma_t^0 \cup \Gamma_u^0$ such that $\Gamma_t^0 \cap \Gamma_u^0 = \emptyset$ in the reference configuration, $\mathbf{b}^0$ is the reference body force, $\bar{\mathbf{t}}^0$ is the surface traction on the Neumann boundary Γ_t^0 , $\bar{\mathbf{u}}$ is the prescribed displacement on the Dirichlet boundary Γ_u^0 , $\mathbf{n}^0$ is the unit outward normal to Γ_t^0 , and H^1 is the first order Hilbert space.

The weak form of the microforce balance Eq. (11) with external microforce $\gamma = 0$ in the total Lagrangian formulation takes the following form

$$\text{Find } \phi \in H^1(\Omega_0 \times (0, T)) \text{ such that}$$

$$\int_{\Omega_0} \delta \nabla \phi \cdot \boldsymbol{\xi} d\Omega = \int_{\Omega_0} \delta \phi \pi d\Omega + \int_{\Gamma_\zeta^0} \delta \phi \zeta d\Gamma \quad (46)$$

satisfying boundary conditions

$$\phi = \bar{\phi} \text{ on } \Gamma_\phi^0 \times (0, T) \quad (47)$$

$$\boldsymbol{\xi} \cdot \mathbf{n}^0 = \zeta \text{ on } \Gamma_\zeta^0 \times (0, T) \quad (48)$$

and initial condition

$$\phi(\mathbf{X}, 0) = \phi_0(\mathbf{X}) \text{ on } \Omega_0 \quad (49)$$

with boundary $\Gamma^0 = \Gamma_\zeta^0 \cup \Gamma_\phi^0$ such that $\Gamma_\zeta^0 \cap \Gamma_\phi^0 = \emptyset$ in the reference configuration, where ζ denotes the microtraction on the Neumann boundary Γ_ζ^0 , $\bar{\phi}$ is the prescribed phase-field parameter on the Dirichlet boundary Γ_ϕ^0 , and $\mathbf{n}^0$ is the unit outward normal to Γ_ζ^0 .

We assume the following finite element discretization of the displacement field

$$\mathbf{u}(\mathbf{X}, t) = N_I(\mathbf{X}) \mathbf{u}_I(t) \quad (50)$$

and order parameter

$$\phi(\mathbf{X}, t) = N_I(\mathbf{X}) \phi_I(t), \quad (51)$$

where $N_I(\mathbf{X})$ is the shape function of node I , $\mathbf{u}_I(t)$ is the nodal displacement, and $\phi_I(t)$ is the nodal order parameter, respectively.

We can write the discrete approximation of the weak form of the Eq. (41) as

$$\mathbf{f}^{ext} - \mathbf{f}^{int} = \mathbf{M} \ddot{\mathbf{U}} \quad (52)$$

where $\mathbf{U}(t)$ is the vector of nodal displacements, $\mathbf{M}$ is the mass matrix, $\mathbf{f}^{ext}$ is the vector of externally applied nodal point loads

$$\mathbf{f}^{ext} = \int_{\Omega_0} \mathbf{H}^T \mathbf{b}^0 d\Omega_0 + \int_{\Gamma_t^0} \mathbf{H}^T \bar{\mathbf{t}}^0 d\Gamma_t^0, \quad (53)$$

where $\mathbf{H}(\mathbf{X})$ is the matrix of shape functions $N_I(\mathbf{X})$. In Eq. (52), $\mathbf{f}^{int}$ is the vector of internal forces corresponding to element stresses

$$\mathbf{f}^{int} = \int_{\Omega_0} \mathbf{B}^T \mathbf{P} d\Omega_0, \text{ where } \mathbf{B}(\mathbf{X}) = \nabla \mathbf{H}(\mathbf{X}). \quad (54)$$

The discretized form of the weak form of the microforce balance Eq. (46) in conjunction with the restriction on π as in Eq. (23) is given as

$$\mathbf{r}(\phi) = - \int_{\Omega_0} \left(\mathbf{N}^T \rho_0 \frac{\partial \psi}{\partial \phi} + \nabla \mathbf{N}^T \boldsymbol{\xi} \right) d\Omega + \int_{\Gamma_\zeta^0} \mathbf{N}^T \zeta d\Gamma = \boldsymbol{\beta} \dot{\phi}, \quad (55)$$

where $\mathbf{N}(\mathbf{X})$ is the matrix of shape functions $N_I(\mathbf{X})$.

The solution of the nodal point displacement and phase-field variable at time ' $t + \Delta t$ ' is obtained using the central difference explicit time integration scheme (Bathe, 1995), for the acceleration $\ddot{\mathbf{U}}$ in Eq. (52) and the evolution of order parameter $\dot{\phi}$ in Eq. (55), i.e.

$${}^t \ddot{\mathbf{U}} = \frac{1}{\Delta t^2} \left({}^{t+\Delta t} \mathbf{U} - 2 {}^t \mathbf{U} + {}^{t-\Delta t} \mathbf{U} \right) \quad (56)$$

and

$${}^t \dot{\phi} = \frac{1}{2\Delta t} \left({}^{t+\Delta t} \phi - {}^{t-\Delta t} \phi \right). \quad (57)$$

If a diagonal mass matrix $\mathbf{M} = \text{diag}(m_{ii})$ is chosen, the solution corresponds to a forward marching in time, where components of the displacement ${}^{t+\Delta t}U_i$ can be explicitly computed as

$${}^{t+\Delta t}U_i = 2{}^tU_i - {}^{t-\Delta t}U_i + \frac{\Delta t^2}{m_{ii}} \left({}^tf_i^{\text{ext}} - {}^tf_i^{\text{int}} \right), \quad (58)$$

where index ‘ i ’ represents the nodal degrees of freedom of the displacement.

Similarly, for the diagonal matrix $\boldsymbol{\beta} = \text{diag}(\beta_{ii})$, the components of the order parameter at time ‘ $t+\Delta t$ ’ is given as

$${}^{t+\Delta t}\phi = {}^{t-\Delta t}\phi + \frac{2\Delta t}{\beta_{ii}} {}^tr_i, \quad (59)$$

where index ‘ i ’ represents the nodal degrees of freedom of the order parameter.

3. Numerical examples

We investigate the effects of shock-induced α - γ phase transformation on the thermomechanical response of RDX using the phase-field model presented in Section 2. A finite element computational model of a bar with dimension $4.0 \times 0.1 \times 0.1 \text{ mm}^3$ is considered to simulate the gas gun tests. The computational domain is discretized using 2,560 tri-linear hexahedral finite elements, each with eight Gauss points. A time varying pressure load is applied to one of the faces normal to the axial direction of the bar, while the opposite face is maintained traction-free. The applied pressure is ramped-up from 0 to 5.2 GPa in 10.0 ns. The four faces of the bar normal to the loading direction are constrained such that a one-dimensional wave could travel along the length of the bar. Artificial viscosity terms have been included for conditioning the numerical solution at the shock front. The same set of parameters has been used for all the loading conditions. Hence, some of the crystal orientations may show ripples at the trailing end of the shock arising from the low order spatial representation.

For the dilatational α - γ phase transformation of RDX, the effect of transformation volume change is computed using a third-order Birch-Murnaghan equation of state (BMEOS) (Eq. (37)), where the pressure-volume relationship for the two phases is distinguished using order parameter. The effect of transformation induced changes in the space group and molecular conformation is captured in the deviatoric stress (Eq. (36)). Hence, in the absence of explicit knowledge of the habit plane, it is reasonable to combine the dilatational transformation with the elastic part of the deformation.

The remainder of this section is organized as follows. The model parameters for both the polymorphs are presented in Section 3.1, followed by discussion on simulation results in Section 3.2.

3.1. Model parameters

α -RDX crystallizes in the orthorhombic space group $Pbca$ (Choi and Prince, 1972), whereas, γ -RDX is orthorhombic with $Pca2_1$ space group (Davidson et al., 2008). The lattice parameters and densities of both the polymorphs are given in Table 1.

Table 1. Lattice parameters and densities.

	α -RDX ^a	γ -RDX ^b
a (nm)	1.3182	1.2565
b (nm)	1.1574	1.0930
c (nm)	1.0709	0.9477
ρ_0 (g/cm ³)	1.8060	2.2680

^aChoi and Prince (1972); ^bDavidson et al. (2008)

The elasticity tensor moduli of α -RDX under ambient condition are taken from the experimental work of Haussühl (2001), whereas, that of γ -RDX at 300K and 5.2GPa are calculated using molecular dynamics simulations (Munday et al., 2011; Josyula et al., 2014). The coefficients of elasticity tensor in Voigt notation and the parameters of third-order Birch-Murnaghan equation of state (BMEOS) for the two polymorphs are given in Table 2. The bulk modulus and the derivative of bulk modulus are obtained by fitting the experimental isothermal volumetric compression data (Olinger et al., 1978) using nonlinear least squares (Munday et al., 2011). The pressure dependent elastic constants for α - and γ -RDX are computed using Molecular Dynamics simulation results reported by Sewell and Bennett (2000), and Josyula et al. (2014), respectively. The constitutive relation for the symmetric Piola-Kirchhoff stress type tensor that incorporates pressure dependent elasticity tensor is presented in Appendix A. The evolution of material parameter with pressure needs to be incorporated in the model in order to capture the physics of high loading rates of RDX (De et al., 2014).

Table 2. Coefficients of elasticity tensor and parameters of third-order Birch-Murnaghan equation of state.

	α -RDX ^a	γ -RDX ^b
C_{11} (GPa)	24.56	80.3
C_{12} (GPa)	7.61	37.8
C_{13} (GPa)	5.30	37.0
C_{22} (GPa)	18.85	67.0
C_{23} (GPa)	5.24	43.9
C_{33} (GPa)	17.33	57.9
C_{44} (GPa)	5.15	11.9
C_{55} (GPa)	4.06	16.3
C_{66} (GPa)	6.90	13.4
K_0 (GPa)	12.10 ^{b,c}	5.5 ^{b,c}
K'_0	8.70 ^{b,c}	16.0 ^{b,c}

^aHaussühl (2001); ^bMunday et al. (2011); ^cOlinger et al. (1978)

The shear modulus $\mu(\phi)$ is calculated using Voigt expression (Schreiber *et al.*, 1973) as

$$\begin{aligned} \mu(\phi) = & \frac{1}{15} [C_{11}(\phi) + C_{22}(\phi) + C_{33}(\phi)] \\ & - \frac{1}{15} [C_{12}(\phi) + C_{23}(\phi) + C_{13}(\phi)] + \frac{1}{5} [C_{44}(\phi) + C_{55}(\phi) + C_{66}(\phi)] \end{aligned} \quad (60)$$

Etching (Connick and May, 1969; McDermott and Phakey, 1971) and indentation (Gallagher et al., 1992; Ramos et al. 2009) experiments identify slip-systems of α -RDX as (010)[001], (010)[100], {011}[010], and {021}[100]. Another slip-system, (001)[010], has been observed from the shock simulation of α -RDX (Cawkwell et al., 2010). The slip-hardening parameters of α -RDX are estimated by curve fitting to the experimental velocity-time trace (De et al., 2014). The slip-systems and -hardening parameters for γ -RDX are not reported in open literature. Therefore, considering similarity in the crystal structures of α - and γ -RDX, same set of slip-systems and -hardening parameters are considered for both the polymorphs. We consider seven major slip-systems, namely, (010)[001], (021)[100], ($0\bar{2}1$)[100], (011)[100], ($0\bar{1}1$)[100], (010)[100], and (001)[100] in our simulation. The temperature rise due to thermoelastic heating is captured using the following temperature-volume equation of state (Menikoff and Sewell, 2002)

$$\theta = \theta_0 [V/V_0]^{-\mathcal{G}}, \quad (61)$$

where V/V_0 denotes volumetric change, $\mathcal{G}$ is a scalar Grüneisen parameter, and $\theta_0 = 300K$ is the initial temperature. The thermal and hardening parameters are listed in Table 3.

The phase-field parameters such as kinetic rate constant for the phase transformation, and interface surface energy are estimated to be consistent with the curve fit to the stress history calculated using experimental data for the shock loading on (111) plane of RDX (Patterson et al., 2007). The interface boundary thickness is assumed to be of the order of nanometer. The phase-field parameters are listed in Table 3.

Table 3. Thermal and hardening parameters.

Specific heat capacity ^{a,b}	$c_v = 1.077 \times 10^{-3} \text{ MJ} \cdot \text{kg}^{-1} \text{ K}^{-1}$
Grüneisen parameter ^c	$\mathcal{G} = 1.103$
Critical resolved shear stress ^d	$\tau_0 = 71.0 \text{ MPa}$
Drag coefficient ^d	$B = 7.0$
Effective damping coefficient ^d	$\dot{\gamma}_{p0} = 1 \times 10^5 \text{ s}^{-1}$
	$n = 0.22$
	$m = 0.03$
Other hardening parameters ^d	$\gamma_0 = 1 \times 10^{-4}$
	$\dot{\gamma}_0 = 1 \times 10^3 \text{ s}^{-1}$
	$\dot{\gamma}_{off} = 6 \times 10^{-2} \text{ s}^{-1}$
	$\lambda = 7.15 \times 10^{-4} \text{ MJ}^{-1} \cdot \text{m}^3$
	$\beta = 8.0 \text{ Js} \cdot \text{m}^{-3}$
Phase-field parameters	$\Gamma = 25.0 \text{ mJ} \cdot \text{m}^{-2}$
	$l = 1.0 \text{ nm}$

^aCawkwell et al. (2008); ^bOlinger et al. (1978); ^cMenikoff and Sewell (2002);

^dDe et al. (2014)

3.2. Results and discussion

We verify the stress history of RDX shocked on the (111) plane with the shock stresses calculated using experimental data for the step loading as shown in Fig. 2 and material properties of α -RDX (Patterson et al., 2007). The stress history is captured at 0.2mm from the impact plane, which corresponds to the midpoint of the sample used for the plate impact experiment (Patterson et al. (2007)). From Fig. 2, we observe that the uniaxial compressive stress vs. time plot for the α - γ phase transformation of RDX agrees with the curve reported in Patterson et al. (2007). The slight deviation from the reported stress-time profile beyond the phase transition stress, i.e. 4.0GPa, can be attributed to the material and structural parameters of the pure α -RDX that are used to calculate the shock stresses in Patterson et al., (2007).

Fig. 2. Comparison of the uniaxial compressive stress σ_{33} (GPa) vs. time t (μ s) plot at a distance of 0.2mm from the impact plane, with the stress history calculated using experimental data for the stepwise shock loading on (111) plane of RDX (Patterson et al., 2007). The inset shows the step loading as a pressure p (GPa) vs. time plot. The dotted red curve shows the simulations with α - γ phase transformation.

Next, we investigate the thermomechanical response of shock-induced α - γ phase transition of RDX loaded on the (100), (210), and (111) planes. From Fig. 3a, and 3c, we observe that the single crystal of RDX shocked on (100) plane undergoes α - γ phase transformation at 4.42GPa for the material point at 1.0mm from the impact plane. In Fig. 3b, two distinct steps in the particle velocity profiles are accompanied by a stress relaxation (Fig. 3c) behind the elastic wave. The stress relaxation may be interpreted as the α - γ phase transformation. The particle velocity profile of α -RDX in Fig. 3f, without considering phase change, is typical for elastic wave. The slightly higher particle velocity in Fig. 3b in comparison with Fig. 3f is due to the larger uniaxial compression associated with the α - γ phase transition, see Fig. 3d and 3h.

Fig. 3. Evolution of (a) phase-field parameter ϕ , (b) particle velocity v_3 (mm/ μ s), (c) compressive stress σ_{33} (GPa), (d) volumetric change V/V_0 , and (e) temperature θ (K) with time t (μ s) for the shock-induced α - γ phase transformation of (100)[001] RDX single crystal. For comparison, the following results are plotted for single crystal of α -RDX shocked on the (100) plane: (f) v_3 vs. t , (g) σ_{33} vs. t , (h) V/V_0 vs. t , and (i) θ vs. t .

We also observe that none of the slip-systems are active for either the α -RDX or α - γ phase change of RDX, implying purely elastic response for this loading orientation. Hence, thermoelastic heating due to volumetric changes predominantly contributes to the temperature evolution. From Fig. 3e and 3i, we see that the peak temperature for α - γ

phase transformation is significantly higher than that of α -RDX, which is due to the larger volumetric compression in case of the former, see Fig. 3d and 3h.

The phase evolution contours in Fig. 4 show that as the shock wave travels along the longitudinal direction of the bar α -RDX transforms to the γ -phase. Notice that the phase evolution slightly lags behind the dilatational wave front, indicating phase transition requires finite time (95ns) to occur. Our simulations suggest that the phase transformation can accommodate larger strain leading to more temperature rise due to volumetric compression as we can see from the temperature evolution contours for the α - γ phase-transformation in Fig. 4, and temperature-time trace in Fig. 3e and 3i.

Fig. 4. Shock-induced α - γ phase transformation of RDX for impact loading on the (100) plane; phase evolution, uniaxial compressive stress (GPa), and temperature (K) are shown at 0.6 μ s.

RDX shocked on (210) plane transforms to the γ -phase at 3.92GPa for the material point at 1.0mm from the impact plane, see Fig. 5a and 5c. The velocity-time trace for α - γ phase transition of RDX in Fig. 5b shows two distinct steps with the stress relaxation associated with the phase change, see Fig. 5c. Whereas, the velocity profile of α -RDX shocked on (210) plane has no discernable precursor, see Fig. 5g. From Fig. 5a, we see that the phase transition requires 126ns to complete.

Unlike the purely elastic (100)[001] loading orientation, RDX shocked on the (210) plane exhibits elastic-plastic response. The slip activity of the two cases, i.e. α - γ phase transition of RDX and α -RDX, without considering phase change, is very similar. Five out of seven known slip systems namely, $\{021\}[100]$, $\{011\}[100]$, and $(010)[100]$ are active for both the cases; with $(010)[100]$ being the dominant slip system and $\{021\}[100]$ being two other dominant slip-systems, see Fig. 6a, and 6b. The slip activation time for α -RDX is marginally longer than that of α - γ phase change. The accumulated plastic slip for α -RDX (Fig. 5i) is significantly larger than that for the α - γ phase change (Fig. 5d). However, the peak temperature is 8% higher for the latter (Fig. 5f), suggesting larger contribution of elastic heating due to volumetric changes (Fig. 5e and 5j), compared to the plastic dissipation. The heating due to volumetric compression

contributes 97% to the total heating for the α - γ phase change in caparison to 74% for the α -RDX.

Fig. 5. Evolution of (a) phase-field parameter ϕ , (b) particle velocity v_3 ($\text{mm}/\mu\text{s}$), (c) compressive stress σ_{33} (GPa), (d) cumulative plastic slip $\bar{\gamma}$, (e) volumetric change V/V_0 , and (f) temperature θ (K) with time t (μs) for shock-induced α - γ phase transformation of

(210)[001] single crystal of RDX. For comparison, the following results are plotted for α -RDX single crystal shocked on the (210) plane: (g) v_3 vs. t , (h) σ_{33} vs. t , (i) $\bar{\gamma}$ vs. t , (j) V/V_0 vs. t , and (k) θ vs. t .

Fig. 6. Evolution of plastic slip along slip systems for (a) α - γ phase transformation of RDX, and (b) α -RDX shocked on (210) plane. The insert shows accumulated slip along active slip systems.

For the shock loading on the (111) plane, α -RDX transforms to γ -phase at 4.0GPa for the material point at 1.0mm from the impact plane (Fig. 7a and 7c) with two distinct steps in the velocity-time trace (Fig. 7b) that is associated with stress relaxation due to phase change (Fig. 7c). The phase transition requires 110ns to complete, see Fig. 7a. Much like the (210) loading orientation, the velocity profile of α -RDX shocked on the (111) plane has no discernable precursor, see Fig. 7g. This behavior may be related to the presence of different plastic deformation mechanisms at higher pressures, where it is hypothesized that the partial dislocation loops nucleate homogenously in the crystal (Cawkwell et al., 2010). These partial dislocation loops are highly mobile and rapidly create stacking fault tetrahedra (SFT) in the lattice. At higher pressure, the homogenously nucleated SFTs act

as obstacles to the glide of perfect dislocations. Hence, materials become very hard and distinct elastic–plastic two-wave structure cannot be observed (Cawkwell et al., 2010). The ripples at the trailing end of the shock in Fig. 7b arise from the combination of low order quadrature rule that is incapable of capturing the discontinuity and presence of phase boundary.

Fig. 7. Evolution of (a) phase-field parameter ϕ , (b) particle velocity v_3 (mm/ μ s), (c) compressive stress σ_{33} (GPa), (d) accumulated plastic slip $\bar{\gamma}$, (e) volumetric change (V/V_0), and (f) temperature θ (K) with time t (μ s) for α - γ phase change of RDX shocked on (111) plane. For comparison, the following results are plotted for α -RDX single crystal: (g) v_3 vs. t , (h) σ_{33} vs. t , (i) $\bar{\gamma}$ vs. t , (j) V/V_0 vs. t , and (k) θ vs. t .

The crystalline slip activities are very different for the two cases in comparison with (100) and (210) loading orientations. While almost all slip systems are active for the α - γ phase transformation (Fig. 8a), only three are active for the α -RDX (Fig. 8b). From Fig. 8, we observe that $\{011\}[100]$ are the two dominant slip-systems for the former, whereas, $(021)[100]$ and $(011)[100]$ slip-systems dominate for the later. The slip activation time for the dominant slip systems in case of the α - γ phase change (Fig. 8a) is significantly longer than that for α -RDX (Fig. 8b). The total accumulated slip on all slip systems is slightly larger for the α -RDX (Fig. 7i) in comparison with the α - γ phase change (Fig. 7d). However, peak temperature is significantly higher for the latter (Fig. 7f and 7k), implying elastic heating due to volumetric compression (Fig. 7e and 7j) dominates over plastic dissipation (Fig. 7d and 7i). For the α - γ phase change heating due to volumetric compression contributes 92% to the total heating in comparison to 84% for the α -RDX.

Fig. 8. Evolution of plastic slip along slip systems for (a) α - γ phase transformation of RDX, and (b) α -RDX shocked on (111) plane.

Overall, our simulations of RDX shocked on (001), (210), and (111) plane show that α -RDX transforms to γ -phase around 3.8-4.5GPa. This is within the experimentally observed range of shock stress 3.5-4.5GPa for α - γ phase change of RDX (Patterson et al., 2007). Phase transformation requires finite time to occur, which is consistent with the experimental observation (Patterson et al., 2007). Phase transition time for the pure elastic orientation (95ns) is less than that of the elastic-plastic orientations (>110ns), which in-turn depends on the extent of plastic deformation. For example, RDX shocked on (210) plane requires 126ns to completely transform to γ -phase, whereas, that on (111) plane takes 110ns, where the former has larger part of plastic deformation. Phase change is also associated with stress relaxation and increased temperature rise compared to pure α -RDX. The peak temperature of the shocked crystal is in the range of 340-386K, which is much below the melt temperature of RDX (477-479K) (Boileau et al., 2009).

RDX impacted on (001), (210), and (111) plane activates 0, 5, and 6 experimentally determined slip systems, respectively. These are the same number of slip systems that are accessible for the aforementioned loading orientations (Gallagher et al., 1992; Ramos

et al., 2009). The seventh slip system (001)[010] is also active for the loading on (111) plane (Fig. 8a), which is in agreement with the molecular dynamic simulation predictions (Cawkwell et al., 2010). Further, inline with experimental observation (Patterson et al., 2007), shock on (111) activates the (010)[001] slip-system (Fig. 8a), whereas shock on (210) does not (Fig. 6a).

4. Conclusions

A thermodynamically consistent phase-field model for shock-induced solid-solid phase transformation of single crystals has been presented. The effects of structural transformation on the deformation mechanisms of shocked single crystal are studied for the α - γ phase transition of RDX. The simulation of gas gun experiments for various crystallographic orientations demonstrate the ability of phase-field model to predict the α - γ phase transition within the experimentally observed range of shock stresses. The shock response of phase transition is orientation dependent. Further, simulations suggest that the phase transition requires finite time to occur. Phase transition time for the elastic orientation is less than that for the elastic-plastic orientations, which in-turn depends on the extent of plastic deformation. Hence, we may conclude that the plasticity tends to delay the phase transition, which may have significant effect on the detonation sensitivity of RDX. The α - γ phase transformation is associated with stress relaxation, and increased temperature rise and associated shock-sensitivity.

The phase-field model presented here can be extended to account for the thermomechanical response of shock-induced solid-solid phase transformation of polycrystalline materials with detailed modeling of grain boundary effects including grain-boundary evolution and grain-size effects. However, such a model requires significant experimental data for calibration.

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