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A phase-field approach to solid–solid phase transformations via intermediate interfacial phases under stress tensor

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ABSTRACT

A thermodynamically consistent phase-field (PF) theory for phase transformations (PTs) between three different phases is developed with emphases on the effect of a stress tensor and interface interactions. The phase equilibrium and stability conditions for homogeneous phases are derived and a thermodynamic potential which satisfies all these conditions is introduced using polar order parameters. Propagation of a solid–solid (*SS*) interface containing nanometer-sized intermediate disordered interfacial phases (*IP*) and particularly an interfacial intermediate melt (*IM*) is studied for an HMX energetic material using the developed PF model. The scale effects (the ratio of widths of *SS* to solid-melt (*SM*) interfaces, k_δ), the effect of the energy ratio of *SS* to *SM* interfaces (k_E), and the temperature on the formation and stability of *IM* are investigated. An interaction between two *SM* interfaces via an *IM*, which plays a key role in defining a well-posed problem and mesh-independent solution, is captured using a special gradient energy term. The influence of the elastic energy on the formation and retainment of *IM* and its structure, hundreds of degrees below the melting temperature, is investigated. Elastic energy promotes barrierless *IM* in terms of an increasing degree of disordering, interface velocity, and width of *IM*, but it surprisingly increases nucleation temperature for the *IM*. The key effect, however, is the drastic reduction (by more than an order of magnitude) of the energy of the critical nucleus of the *IM* within the *SS* interface, which is caused by the elastic energy. The developed PF model is applicable for the general case of PT between three phases and can be applied (adjusted) to other physical phenomena, such as premelting/disordering at grain boundaries, martensitic PTs, surface-induced premelting and PTs, and developing the interfacial phase diagrams.

1. Introduction

The formation and stabilization of *IP* (e.g., surfacial amorphous films and intergranular amorphous films) have many important applications, e.g., in the electronic industry (Luo and Chiang, 2008). Interfacial phases also play an important role in sintering, alloying, and strengthening ceramic materials (Luo et al., 1999; Becher et al., 2000). In addition, the properties of *IP* are different from the constituent homogeneous phases. A sample with a large volume fraction of *IP* shows different overall properties (e.g. creep, superplasticity, and electrical conductivity), compared to the sample of homogeneous phases (Cantwell et al., 2014). Therefore, any advancement in the theoretical and computational modeling of *IP* can have a significant scientific and industrial impact.

Interfaces between different phases can undergo PTs similar to bulk materials and can be treated as quasi-two-dimensional phases. The chemical and structural properties of the interfaces change abruptly or continuously during their PT during a variation of the corresponding driving forces. Although the interfaces can be analyzed using equilibrium thermodynamics, the equilibrium *IPs* have varying properties. The Gibbs definition of a phase cannot be applied because of its inhomogeneous structure and composition (Cantwell et al., 2014). The presence of *IPs* can change thermodynamic properties of materials and can lead, for example, to liquid-metal embrittlement (Luo et al., 2011). It also alters the kinetics of processes, e.g., PTs and grain growth (Dillon et al., 2007). Interfacial phases emerge in a wide range of processes such as premelting and prewetting, surface-induced premelting and PT (Levitas and Samani, 2011a,b; Levitas and Javanbakht, 2011,

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2010), intrinsic PT that occurs in pure materials, and extrinsic PT that happens in non-pure materials involving an adsorption of an impurity or dopant (Frolov et al., 2013; Frolov et al., 2013).

Solid–solid PT via a nanometer-sized intermediate disordered *IP* called intermediate melt, *IM*, at temperatures much below melting temperature (θ_e^m) has been predicted thermodynamically (Levitas et al., 2004, 2006; Levitas, 2005; Levitas et al., 2012) and confirmed experimentally for an HMX energetic material (Smilowitz et al., 2002; Henson et al., 2002; Levitas et al., 2004, 2006), $PbTiO_3$ piezoelectric nanowires (Levitas et al., 2012), and for amorphization in an insulin enhancer pharmaceutical substance called avandia (Randzio and Kutner, 2008). The PT via formation of *IM* was also suggested as the mechanism for crystal-crystal PT and amorphization for materials with reducing melting temperature under pressure (e.g., ice, Si, and Ge) (Levitas, 2005). Furthermore, stresses may also be due to an applied external loading. Formation of *IM*under a high strain rate loading was predicted thermodynamically and confirmed using MD simulations for aluminum and copper (Levitas and Ravelo, 2012).

The thermodynamic condition for the appearance of an *IM* between solid-1 and solid-2 (S_1MS_2 interface) is $E^{21} - E^{10} - E^{20} - E^e > (G^0 - G^s)\delta^*$ (See Ref. (Levitas and Momeni, 2014)). Here, E^{10}, E^{20}, and E^{21} are the energies of the S_1M, S_2M, and *SS* interfaces, respectively; E^e is the elastic energy of the coherent *SS* interface; δ^* is the width of the *IM*, and G^0 and G^s are the bulk thermal energies of melt and the solid phase with a smaller melting temperature θ_e^m, respectively. Reduction of the total interface energy and relaxation of the elastic energy are the driving forces for the formation of melt significantly below θ_e^m. Theoretical models based on the sharp-interface approach (Levitas et al., 2012, 2006; Levitas, 2005; Levitas et al., 2004) have neglected the change in interface energy during melting as well as the interfacial interactions. The main driving force for the formation of *IM* in these models was the relaxation of internal stresses due to large volumetric transformation strains. This driving force vanishes as soon as melt forms which results in a supercooled melt and immediate resolidification of melt to the stable solid phase. This intermediate transient melt is a special form of *IM*which is called virtual melt (Levitas et al., 2004, 2006). Formation of the virtual melt is predicted in materials with large volumetric transformations that generate large elastic energy when other stress relaxing mechanisms, such as plastic deformation and twinning, are suppressed; e.g., in materials with complex molecular or atomic structures.

Different techniques are utilized for characterizing and modeling the *IP*. The developed models, based on the sharp-interface approach which considers zero-thickness interfaces, are oversimplified because the *IP*has a width in the range of a few nanometers, which is comparable with the width of a *SS* interface. Furthermore, a sharp-interface approach considers a bulk phase sandwiched between two interfaces of zero-thickness and cannot capture formation of the *IP*with partial melting. Molecular dynamics (MD) simulations have been utilized to investigate interfacial PTs in pure materials (Frolov et al., 2013). However, investigating such PTs in multiphase materials using the MD technique is limited by an inevitable long simulation time for producing equilibrated composition profiles. Properties of *IP* have also been studied using *ab initio* techniques (Painter et al., 2002; Rulis et al., 2005; Shibata et al., 2004). A phase-field crystal model (Elder and Grant, 2004) was also used to investigate the effects of *IP*, such as grain boundary premelting (Mellenthin et al., 2008).

An advanced PF approach to formation of the *IM* was developed in Ref. (Momeni and Levitas, 2014) but without mechanics. The interaction between two *SM* interfaces through melt are modeled using an *SS* interface energy contribution within complete melt. A new force-balance model was introduced that could match the results of PF simulations up to temperatures significantly below the melting temperature. Shifting from a jump-like first-order type to a continuous second-order type PT that are separated by an *IM*-free region was captured during *IM*-formation as k_δ reduced. The presence of three solutions associated with stable and metastable *IM*, as well as a critical nucleus (CN) of *IM* were revealed. A retainment of *IM* at temperatures significantly below melting temperature for $k_E < 2.0$ was also illustrated. The dependence of the interface energy on a_0 and k_δ in the presence of *IM* was demonstrated using the numerical simulations.

The *goal* of this paper is to generalize a model (Momeni and Levitas, 2014) for the case when elastic energy and stresses are important. An advanced PF approach to PTs with a strong focus on the effect of the stress and transformation strain tensors has been developed for martensitic PT (Levitas et al., 2003; Levitas and Preston, 2002a,b; Levitas et al., 2009; Cho et al., 2012; Levitas, 2013), surface-induced PT in solids (Levitas and Javanbakht, 2011, 2010), melting (Slutsker et al., 2006; Levitas and Samani, 2011a,b), dislocation evolution (Levitas and Javanbakht, 2013, 2015b), and the interaction between PT and dislocations (Levitas and Javanbakht, 2012, 2014, 2015a,b, Javanbakht and Levitas, 2015). Here, a thermodynamically consistent phase field approach for *IM* at the *SS* interface under a general stress tensor will be developed, combining our PF approaches to PT in solids, melting, and the model (Momeni and Levitas, 2014) without mechanics. Some preliminary simulations with mechanics have been presented in short communications in Ref. Levitas and Momeni (2014) and Momeni et al. (2015).

The remainder of this paper is organized as follows. In Section 2, a strict thermodynamic approach is developed for the free energy potential that depends on the polar order parameters and their gradients, as well as elastic strain and temperature. The constitutive equations are derived for the general case of a three-phase material under a stress tensor. Specific expressions for the Helmholtz free energy and thermal and transformation strains are presented, which (as we will show in Section 4) satisfy all the formulated thermodynamic equilibrium and stability conditions for homogeneous states. The time-dependent GL equations are derived in Section 3 for a nonequilibrium propagating interface. In Section 4 thermodynamic stability conditions are derived in the general form and for our specific model. A detailed description of the numerical implementations of the model, including the initial conditions used to study the kinetics and capture the CN, are described in Appendix. The developed model is then specified for the properties of an HMX energetic material, and the effects of different parameters on the formation of *IM* and *SS* PT are studied in Section 5. In Section 6, formation and structure of the CN of *IM* within the S_1S_2 interface and CN of the S_1S_2 interface within the S_1MS_2 interface are studied in detail for the models with and without mechanics. Finally, the results of this study are summarized in Section 7.

We have designated the contraction of tensors $\boldsymbol{A}$ and $\boldsymbol{B}$ over one and two indices with $\boldsymbol{A} \cdot \boldsymbol{B}$ and $\boldsymbol{A} : \boldsymbol{B}$, respectively. The subscripts *s* and *a* label the symmetric and the skew-symmetric part of a second-rank tensor. The unit tensor and Kronecker delta are designated by $\boldsymbol{I}$ and δ_{ij}, respectively; $\boldsymbol{\nabla}$ is the gradient operator.

2. Thermodynamic theory

2.1. Polar order parameters

Following Refs. Levitas et al. (2003) and Momeni and Levitas (2014), the polar order parameters, the radial Υ and the angular ϑ, are introduced in a plane (Fig. 1). Geometrically, $\pi\vartheta/2$, is the angle between the radius vector $\boldsymbol{\Upsilon}$, and the axis 1. The origin of