

Computational Modeling with a New Lattice-Based Continuum Formulation for the Coupled Thermodynamic and Mechanical Equilibrium of Polycrystalline Solids

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ABSTRACT

A new formulation and computational framework is presented for modeling coupled self-diffusion and mechanics in polycrystalline materials. The continuum formulation includes constitutive models derived from lattice-level thermodynamic and mechanical considerations. From a complete statement of the change in free energy with respect to changes in strain and concentrations of atoms and vacancies, constitutive equations for both stress and chemical potential are derived in a consistent manner. Advanced finite element methods are used for stable solution of the system of governing equations. An example demonstrates stress-mediated creep due to vacancy diffusion.

Keywords: thermodynamics, continuum mechanics, self-diffusion, creep, finite element methods.

INTRODUCTION

The properties and behavior of polycrystalline thin films may depend crucially on the grain boundary structure, especially as feature size approaches grain size. For many problems of technological interest, such as hillock formation and electromigration in metal films, the consideration of several coupled physical phenomena is required. The motivation for this work is to provide a sufficiently general model that will enable the treatment of arbitrary boundary value problems. This is to be contrasted with previous treatments in an analytic, 1D framework [1-3] or on simple, regular domains [4]. For the latter case, tractable elasticity solutions are adopted to calculate the stress.

The formulation presented is based on lattice-level thermodynamic and mechanical considerations and provides continuum-level constitutive equations. Similarities exist with respect to the models of Larche [5,6]. However, the thermodynamic basis is more detailed and complete for this problem. The constitutive equations for both chemical potential and stress allow for different properties in regions of high disorder where sources and sinks for vacancies are active (i.e. grain boundaries and dislocation clusters) and in defect-free regions of grains.

COUPLED PROBLEM MECHANICS

Thermodynamic Formulation

Constitutive equations for chemical potential μ_v or stress σ can be derived from a change in free energy with respect to a change in concentration of vacancies or strain. Gibbs free energy is defined as

$$\mathcal{G} \equiv E_{int} - W - TS \quad (1)$$

Where \mathcal{G} , the internal energy E_{int} , the work done W , and the entropy S are quantities per unit volume and T is the temperature. A change in Gibbs free energy of a system occurs with a change in the concentrations of atoms C_a , vacancies C_v (numbers per unit volume) or strain ε .

The key to the full coupling in this formulation lies in the modification of the standard (elastic) stored energy. In any crystalline solid there is a temperature-dependent equilibrium concentration of vacancies, denoted C_{vo}^{eq} , in the stress-free lattice. Any deviation from this concentration causes volumetric stress. Additionally, atoms may accumulate or be depleted in regions of disorder and cause further change θ_a in volumetric stress. This is manifested as diffusional creep. The internal energy has been formulated to reflect this in its volumetric component:

$$\begin{aligned} E_{int} &= \hat{E}_{int}(\varepsilon, C_a, C_v, T) \\ &= \frac{1}{2} \kappa [\text{tr}(\varepsilon) + (1-f)\Omega_a(C_v - C_{vo}^{eq}) - \theta_a]^2 \\ &\quad + G [\text{dev}\varepsilon : \text{dev}\varepsilon] + C_v e_f^{bond} + \hat{E}_T. \end{aligned} \quad (2)$$

Here κ and G are the bulk and shear moduli and e_f^{bond} is the energy of bond formation of a single vacancy. The volume of an atom, Ω_a , is not assumed constant; rather, $\Omega_a = \Omega_{a_o} [1 + \text{tr}(\varepsilon)]$. The relaxed volume of a vacancy is denoted $f\Omega_a$. The term \hat{E}_T represents a thermal contribution which is not a function of composition or strain. Below, expressions will be simplified with the definition

$$\varepsilon_{vol} = \text{tr}(\varepsilon) + (1-f)\Omega_a(C_v - C_{vo}^{eq}) - \theta_a. \quad (3)$$

The incremental work done is

$$\hat{W}(\varepsilon, C_a, C_v) = -t_n [\Omega_a (\Delta C_a + f \Delta C_v)] \chi \quad (4)$$

where the terms in brackets represent the strain change associated with the addition of atoms and vacancies to the system at an interface. Such a volumetric strain does work against the normal traction on the interface, $t_n = \mathbf{n} \cdot \mathbf{t}$, where $\mathbf{t} = \sigma \mathbf{n}$. This term is multiplied by the position and time dependent indicator function $\chi(\mathbf{x}, t)$ which specifies the regions over which this work term is active. In the bulk of grains $\chi = 0$, and in a grain boundary or region of high defect density $\chi = 1$.

The configurational entropy is

$$\begin{aligned} S_{conf} &= \hat{S}_{conf}(C_a, C_v) \\ &= k [C_L \log C_L - C_a \log C_a - C_v \log C_v] \end{aligned} \quad (5)$$

where $C_L = C_a + C_v$ is the concentration of lattice sites. The exact form of the vibrational entropy \hat{S}_{vib} will not be important in what follows since it is a function of neither composition nor strain.

Constitutive Equations

The chemical potential of vacancies is the derivative of the Gibbs free energy with respect to the concentration of vacancies:

$$\mu_v \equiv \frac{\partial \mathcal{G}}{\partial C_v} + \frac{\partial \mathcal{G}}{\partial C_a} \frac{dC_a}{dC_v} + \frac{\partial \mathcal{G}}{\partial C_L} \frac{dC_L}{dC_v}. \quad (6)$$

We assume that the addition of atoms to the system at boundaries causes only an increase in lattice sites, $dC_L = dC_a$ (i.e. the number of vacancies is unchanged in this process). Likewise the addition of vacancies does not change the number of atoms so $dC_L = dC_v$ in this case. However, in the bulk the concentration of lattice sites does not change with composition, i.e. $dC_L = dC_a + dC_v = 0$. The indicator function χ allows combination of these two cases into a single expression for μ_v . This expression is simplified by substituting the equilibrium concentration of vacancies at zero stress, C_{vo}^{eq} . The condition $\mu_v = 0$ (with $\varepsilon_{vol} = 0$ and $t_n = 0$) corresponds to this equilibrium and results in the definition

$$C_{vo}^{eq} = C'_{Lo} \exp\left(\frac{-e_f^{bond}}{kT}\right) \quad (7)$$

C'_{Lo} is the stress-free concentration of atoms (lattice sites) in the bulk (in a disordered region). Combining (1)–(7),

$$\begin{aligned} \mu_v &= \kappa \varepsilon_{vol} (1 - f) \Omega_a - t_n f \Omega_a \chi \\ &\quad + kT \ln[1 + \text{tr}(\varepsilon)] + kT \ln \frac{C_v}{C_{vo}^{eq}} \end{aligned} \quad (8)$$

The stress tensor is the derivative of the Helmholtz free energy with respect to strain. Helmholtz free energy is defined as

$$\Psi = E - TS = \mathcal{G} + p \Delta V \quad (9)$$

Using (1),

$$\begin{aligned} \sigma &\equiv \frac{\partial \hat{\Psi}}{\partial \varepsilon} \\ &= \kappa \varepsilon_{vol} [1 + (1 - f) \Omega_{a_o} (C_v - C_{vo}^{eq})] \mathbf{1} \\ &\quad + 2G \text{dev} \varepsilon \end{aligned} \quad (10)$$

Vacancy Flow

The continuity equation governs the flow of vacancies. Vacancies are created and destroyed in regions of high disorder, i.e. grain boundaries and dislocation clusters, where $\chi = 1$. In these regions, vacancy concentrations go to the equilibrium concentration C_v^{eq} which is a non-linear function of the normal stress on the boundary. This is reflected by a source term in the mass balance equation for vacancies:

$$\frac{\partial C_v}{\partial t} = -\nabla \cdot \mathbf{J}_v - \frac{1}{\tau} (C_v - C_v^{eq}) \chi \quad (11)$$

where τ is a time constant that defines the temporal response of the source; $\tau \rightarrow 0$ means that vacancies instantaneously go to their equilibrium values. The value for C_v^{eq} is determined by iterative solution of the condition $\mu_v|_{C_v=C_v^{eq}} = 0$. With μ_v as in (8), the flux of vacancies is

$$\mathbf{J}_v = -\frac{D_v C_v}{kT} (\nabla \mu_v - \mathcal{E} q^*) \quad (12)$$

\mathcal{E} is the electric field defined as the negative gradient of the electrical potential, $\mathcal{E} = -\nabla \phi$. The empirical constant q^* is the apparent charge of a vacancy in an electric field. Note that the strain explicitly appears in μ_v

Mechanical Equilibrium

Mechanical equilibrium requires

$$\nabla \cdot \sigma = \mathbf{0} \quad (13)$$

with σ as in (10). Note that C_v appears in σ explicitly and within ε_{vol} . Likewise for the mass balance equation, ε is in μ_v explicitly and in ε_{vol} . Thus, with the constitutive equations, the system of equations (11) and (13) is fully coupled.

NUMERICAL METHODS

The numerical implementation of the coupled formulation is achieved with a staggered finite element scheme. The vacancy concentration is governed by the continuity equation (11) which is in advection-diffusion form. Such equations require stabilization to prevent spatial oscillations in the numerical solution. However, in this case, standard advanced stabilization methods [7] would require impractical computations with the strong form of this equation. Here a modified method based on the dominant advective terms has proven effective.

Determination of C_v^{eq} for the source term in (11) requires the solution of a transcendental equation. This, as well as flux terms which consist of high-order polynomial terms, render the flow problem nonlinear.

EXAMPLES AND VALIDATION

Numerical examples demonstrate the physical basis and computational robustness of the approach. The computational methods implemented permit the inclusion of physically realistic material property variations across grain boundary regions. The example shown contains a relatively large grain boundary region for the purpose of visualization of concentration and stress variations.

A model problem representing a single grain in a polycrystalline structure illustrates the dependence of the equilibrium concentration of vacancies on the spatially-varying formation energy of vacancies (Figure 1) and, within the source/sink region near the surface, on the normal component of stress (Figure 2). In addition to the pure shear stress state resulting from applied tractions, the converged solutions to the coupled problem show hydrostatic self-stresses which are induced in the material as a result of vacancy diffusion (Figure 3). The steady-state vacancy flux (equal to the negative of atomic flux) in the converged solution is shown in Figure 4. Three sources of vacancy flux may be identified in the formulation: concentration gradients as in Fick's Law, stresses arising from externally applied tractions, and self-stresses resulting from changes in vacancy and atom concentration. The progressive buildup of atoms at the top and bottom surfaces under normal tension and the depletion of atoms on the side surfaces under normal compression results in creep behavior in the material.

The average creep rates shown in Figure 5 are $-5.30 \times 10^{-8} \text{ s}^{-1}$ in the horizontal direction and $-4.47 \times 10^{-8} \text{ s}^{-1}$ in the vertical direction. These compare favorably with the value $\dot{\epsilon} = \pm 3.3 \times 10^{-8} \text{ s}^{-1}$ obtained for the strain rates using the Nabarro-Herring creep equation [8]

$$\dot{\epsilon} = \frac{2\sigma\Omega_a D_a}{kTL^2} \quad (14)$$

with the values for aluminum used in this example: $T = 473\text{K}$; $\sigma = \pm 60 \text{ MPa}$; $\Omega_a = 1.67 \times 10^{-23} \text{ cm}^3$; $D_a = 1.08 \times 10^{-7} \text{ } \mu\text{/s}$ (from activation energy of 1.28 eV); $L = 1 \text{ } \mu$; $e_{f,grain}^{bond} = 0.67 \text{ eV}$; $e_{f,g.b.}^{bond} = 0.576 \text{ eV}$. These values are significantly lower than experimentally determined values [9], indicating that other mechanisms of creep are more significant. Increasing the diffusivity in the grain boundary region results in higher strain rates and perhaps captures the effect of Coble creep. Other mechanisms involve plastic flow, which has not yet been incorporated in the formulation. This work is a foundation on which more complicated constitutive relations for stress may be implemented in order to model such mechanisms.

CONCLUSIONS

A complete thermodynamic foundation for modeling a lattice subject to compositional and mechanical changes has been presented. The constitutive equations reflect the full coupling of vacancy flow and mechanical equilibrium. The chemical potential and flow equation reflect different behaviors in the bulk of grains and in grain boundaries. In addition to instantaneous strain, applied tractions cause progressive creep deformation via diffusion.

This work forms the first step toward general mathematical and computational models for self-diffusion in polycrystalline thin metal films.

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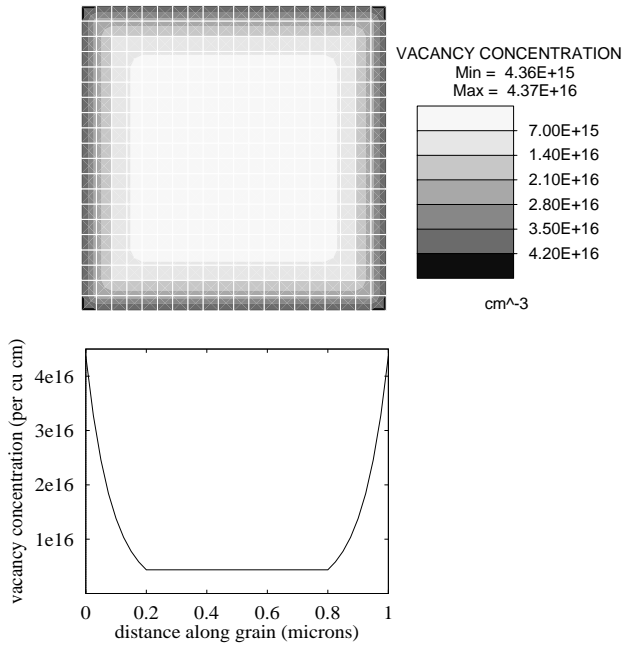


Figure 1: Schematic grain with zero external tractions showing (steady state) constant concentration of vacancies in the bulk of the grain and concentration of vacancies exponentially increasing toward the surface of grain (center of grain boundary). The solution results from a prescribed linear increase in the formation energy of vacancies toward the surface in the outer region shown by the dashed line. Lower plot shows concentration profile across center of grain.

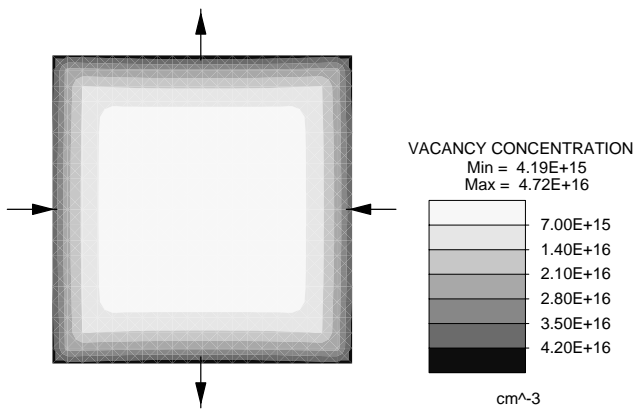


Figure 2: Equilibrium vacancy concentration in grain subjected to pure shear stress just after tractions are applied.

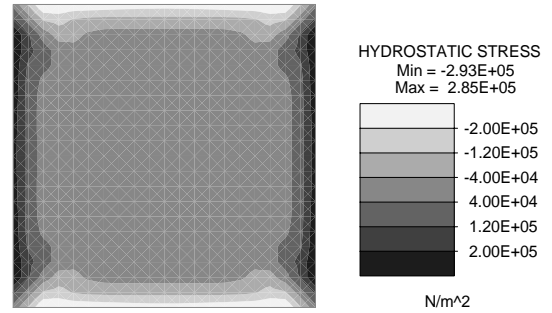


Figure 3: Hydrostatic self-stress induced by the movement of vacancies in the lattice.

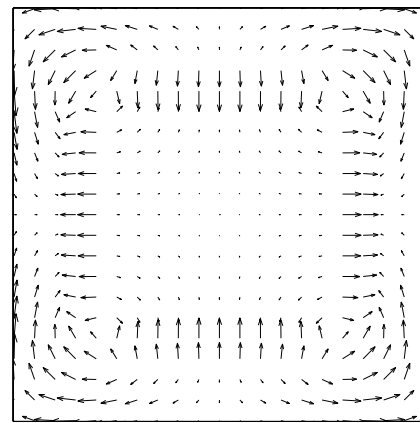


Figure 4: Arrows show flux in the schematic grain.

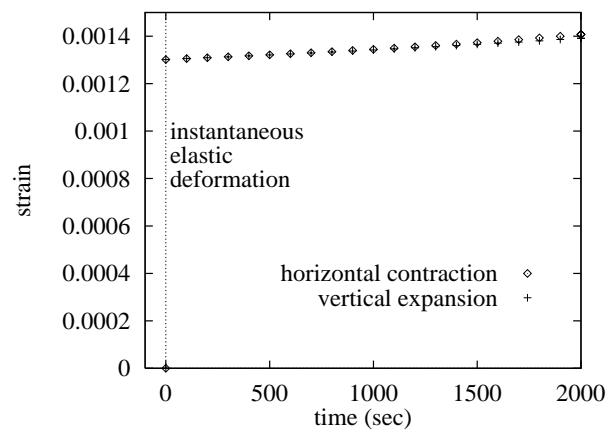


Figure 5: Creep rate is shown by the slopes of y-direction extension and x-direction contraction vs. time.