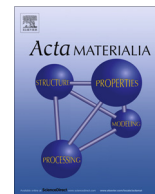




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Stabilization of nanocrystalline alloys via grain boundary segregation: A diffuse interface model

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ABSTRACT

Recent experimental and theoretical findings suggest that nanocrystalline binary alloys can be stabilized against interface-driven homogenization processes via grain boundary (GB) solute segregation mechanism. However, a detailed understanding of this process requires detangling the thermodynamic aspect, GB energy, from the kinetic one, GB mobility. In this work, we present a diffuse-interface model of GB segregation in binary metallic alloys that is capable of accounting for bulk thermodynamics, interfacial energies, and the interaction of alloying elements with GBs. In addition, the model presented herein extends current treatments by independently treating solute–solute interactions within both the bulk grain and GB regions, allowing for deviations from dilute and ideal systems and the ability to account for phase separation processes occurring in conjunction with grain growth. Starting with the analytical treatment of one-dimensional (1D) systems, we investigate the dependence of the GB energy, and subsequently the driving force for grain growth, on the segregation model parameters. More specifically, classic GB segregation isotherms are recovered in the limit of 1D infinite grains. Simulation results of two-dimensional systems reveal regimes of increased thermal stability, and highlight the importance of the thermodynamic model parameters of both bulk grain and GBs on grain growth processes. In broader terms, our modeling approach provides further avenues to explore GB solute segregation and its role in stabilizing polycrystalline aggregates.

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1. Introduction

Owing to their nanometric characteristic feature size, nanocrystalline materials (NCs) exhibit a unique combination of properties [1–4] that render them an attractive choice in applications ranging from industrial and biomedical to optical and nanoelectronics [5–7]. In conventional microstructural materials, only a small fraction of atoms is spatially located at or in the immediate vicinity of grain boundaries (GBs). On the other extreme, NCs are characterized by a large content of GBs, with many atoms residing near interfaces [1,6,8]. This interfacial contribution is considered an Achilles' heel for any potential large scale commercialization as NCs are highly unstable against grain growth and coarsening processes even at low service temperatures [9–13]. These interface-driven processes lead to reduction in the total free energy, ΔG , via the decrease in the total interfacial area and/or the reduction in interfacial energy due to changes in the geometrical attributes of the interface, i.e., $\Delta G \sim \Delta(\gamma A)$ [14]. The development of NC alloys

with increased stability against grain growth is necessary to increase their competitiveness *viz-à-viz* other materials systems, especially in applications with harsh operating environments and elevated temperatures.

In the case of thermally driven grain growth and in accordance with the Gibbs–Thomson equation, the normal velocity, \mathcal{V}_n , at any point on the GB is given by [14,15]

$$\mathcal{V}_n = M_{gb} P_o = M_{gb} \gamma_{gb} \mathcal{K}, \quad (1)$$

where M_{gb} is the boundary mobility and P_o is the driving force for grain growth, γ_{gb} is the GB energy, and \mathcal{K} is the local mean curvature. Broadly speaking, there are two main routes to stabilizing NCs against grain growth [9,16,17]. The first is the kinetic approach in which GB mobility is hindered via solute drag [18–20], or by pinning mechanisms due to a dispersion of closely spaced second-phase particles, commonly known as Zener pinning [21,22]. On the other hand, thermodynamic stabilization occurs via the introduction of alloying elements into a polycrystalline material, which preferentially segregate to GBs; a process that results in reduction in the GB energy and thus the driving force for grain growth [16]. In fact, the reduction of interfacial energy via

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adsorption of solute atoms/active agents is commonly utilized in the study of fluid–fluid interfaces [23,24]. Indeed, the Gibbs adsorption isotherm relates the surface density of solute at the interface (excess solute), Γ , to changes in the interfacial energy, γ , with respect to the solute chemical potential, μ . This is quantified by [25]

$$\Gamma = - \left(\frac{\partial \gamma}{\partial \mu} \right)_{P,T}, \quad (2)$$

where the partial differentiation is evaluated at constant pressure P and temperature T . An alloying element that results in a reduction in GB energy via increasing its chemical potential will ultimately accumulate at the GB [25]. Classical adsorption (segregation) isotherms relate the solute concentration at the interface to the one in the bulk material far from interfaces. The so-called Langmuir–McLean isotherm [26] is considered the first treatment of equilibrium segregation at solid interfaces and it assumes that GB positions are substitutional sites, which are equally available for segregation [25,27]. On the other hand, the Guttman isotherm [28] deals with non-ideal multicomponent systems and it accounts for various types of solute–solute interactions at the GBs. The Fowler–Guggenheim isotherm [29] is considered a special case of the Guttman model that applies to non-ideal binary metallic alloys [25].

Within the context of polycrystalline materials, Weissmüller [30] studied the thermal stability of nanostructures and the interaction of alloying elements with topological defects. Assuming a dilute system and utilizing the McLean isotherm, Weissmüller derived an analytical expression for the reduction in GB energy in terms of the GB heat of segregation [30]. Experimentally, several studies on binary NCs that are based on Ni [31–33], Cu [10,34], Fe [35,36], W [37], and Pd [38] have been conducted to examine grain growth and thermal stability in the presence of GB solute segregation. In all of the aforementioned experimental work, it was observed that the proper choice of the alloying element, resulting in a positive heat of segregation, leads to nanostructures with increased thermal stability. Moreover, it was suggested that the reduction in GB energy by virtue of solute segregation to GBs is the underlying mechanism for the observed stabilization. Others propose that the thermodynamic and kinetic routes are deeply intertwined and both act simultaneously, where their degree of influence is dictated by the segregation and diffusion of solute atoms to GBs [7,10,34]. Recently, stability maps have been constructed for various combinations of binary elements to infer information on the energetics of GB segregation and thermal stability of these alloys [39–41].

Analytical and thermodynamic treatments of binary NCs have been developed to relate GB energy to segregation energetics [17,40,42]. Typically, these studies utilize the regular solution approximation in combination with the Gibbs adsorption equation to derive simple relations for the dependence of GB energy on thermodynamic parameters. Atomistic studies provide valuable insights on the preferential GB sites for segregation and anisotropic effects but are unable to attain diffusive time scales associated with homogenization processes [32,43–46]. At the mesoscale, modeling efforts are focused on investigating solute drag in dilute systems and have been successfully mapped onto classic treatments of solute drag [47–51]. Motivated by the work of Grönghagen and Ågren [48], Kim and Park [49], assuming an ideal solution with bulk concentration $c = 0.01$, examined the shrinking kinetics of an isolated grain embedded in a matrix grain in the presence of GB segregation. In their study, the McLean isotherm was utilized to investigate the role of atomic diffusivity on the evolution of the circular grain and concentration profile. Recently, Heo et al. [51] extended the framework detailed in [47,48] to account for strain-induced GB segregation and the resulting solute drag effects.

While these treatments provide useful insights on the role of GB segregation on grain growth, they only examine the kinetic aspect of GB segregation, i.e., solute drag, and do not account for solute–solute interactions within GBs or deviations from ideal and dilute systems [47–51].

In this work, we develop a theoretical and computational phase field framework for the microstructural evolution of binary NCs with the aim of quantifying the thermodynamic aspects of GB segregation. We investigate, in a parametric study, the role of various thermodynamic parameters on grain growth dynamics. Starting with one dimensional systems, the equilibrium properties are derived and the dependences of the GB energy and width on model parameters are described. Next, we survey through simulations of two-dimensional systems the phase-space of model parameters and reveal regimes with increased thermodynamic stability. The rest of the manuscript is organized as follows: The theoretical modeling framework is presented in Section 2, while the equilibrium properties and the resulting GB segregation isotherms are presented in Section 3. Simulation results of various two-dimensional systems are presented and discussed in Section 4. Finally, this manuscript is concluded by Section 5, which provides a summary and discusses our future work on this model.

2. Theoretical framework

The starting point of our phase field model is the introduction of structural order parameters (OPs) $\{\phi_i(\mathbf{r}, t), i = 1, \dots, n_\phi\}$ that describe grains in an alloy with various crystallographic orientations. Here, \mathbf{r}, t, n_ϕ denote the position vector, time and number of OPs needed to resolve the microstructure, respectively. In this study, we focus on binary metallic alloys of substitutional elements A (host) and B (solute), where a conserved solute concentration field $c = c(\mathbf{r}, t)$ is defined throughout the alloy. Next, we propose the following for the total free energy functional, \mathcal{F}_{tot} , of a polycrystalline binary alloy

$$\mathcal{F}_{tot} = \int d\mathbf{r} f_{tot}(c, T, \phi_i) = \int d\mathbf{r} \left[f_{mix}(c, T) + W_\phi f_{grain}(\phi_i) + \sum_i \frac{\epsilon_i^2}{2} |\nabla \phi_i|^2 - f_{inter}(c, \phi_i) \right], \quad (3)$$

where f_{mix} is the homogeneous free energy density, $f_{grain}(\phi_i) = f_{grain}(\{\phi_i(\mathbf{r}, t), i = 1, \dots, n_\phi\})$ is the free energy density of the grain microstructure and W_ϕ is a parameter that sets the energy scale. The third term on the right hand side of Eq. (3) describes GB energy, where under the isotropy assumption $\epsilon_i = \epsilon$. This assumption will be invoked for the remainder of this study, but could be generalized in future work. Also, one could add to f_{tot} an additional term $f_{phase} = (\kappa^2/2) |\nabla c|^2$ to account for the interfacial energy due to compositional domains in phase-separating systems, where κ is a model parameter that sets the energy of phase boundaries between A-rich and B-rich domains. $f_{inter}(c, \phi_i) = f_{inter}(c, \{\phi_i(\mathbf{r}, t), i = 1, \dots, n_\phi\})$ is an interaction term that couples the solute concentration field, $c(\mathbf{r}, t)$, to the grain microstructure and whose explicit form will be discussed further below. Under the regular solution approximation, the homogeneous free energy density is written as

$$f_{mix} = G_B c + G_A (1 - c) + \frac{RT}{V_m} [c \ln c + (1 - c) \ln(1 - c)] + \Omega c (1 - c), \quad (4)$$

where G_B and G_A are the free energy densities in pure states, R, T, V_m , and Ω are the ideal gas constant, temperature, molar volume (assumed the same for A and B elements), and enthalpic term coefficient (heat of mixing), respectively. The OPs are conveniently chosen such that the equilibrium values within a grain

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