Computational Materials Science 81 (2014) 493–502

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Characterizing solute segregation and grain boundary energy in binary alloy phase field crystal models

Jonathan Stolle [a,*], Nikolas Provatas [b]

[a] Department of Physics and Astronomy, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S-4L7, Canada
[b] Department of Physics, Centre for the Physics of Materials, McGill University, 3600 Rue University, Montreal, Quebec H3A-2T8, Canada

ARTICLE INFO

Article history:
Received 15 April 2013
Received in revised form 26 July 2013
Accepted 2 September 2013
Available online 7 October 2013

Keywords:
Phase field crystal modelling
Binary alloy
Grain boundary energy
Grain boundary segregation

ABSTRACT

This paper studies how solute segregation and its relationship to grain boundary energy in binary alloys are captured in the phase field crystal (PFC) formalism, a continuum method that incorporates atomic scale elasto-plastic effects on diffusional time scales. Grain boundaries are simulated using two binary alloy PFC models – the original binary model by Elder et al. [18] and the XPFC model by Greenwood et al. [25]. In both cases, grain boundary energy versus misorientation data is shown to be well described by Read–Shockley theory. The Gibbs adsorption theorem is then used to derive a semi-analytic function describing solute segregation to grain boundaries. This is used to characterize grain boundary energy versus average alloy concentration and undercooling below the solidus. We also investigate how size mismatch between different species and their interaction strength affects segregation to the grain boundary. Finally, we interpret the implications of our simulations on material properties related to interface segregation.

1. Introduction

Microstructure in metals is important for determining many of their properties (e.g., mechanical, thermal, electrical). The various defects associated with microstructure formation (e.g., grain boundaries, dislocations, vacancies) contribute to an excess of free energy of a system. As a material evolves towards equilibrium, its microstructure changes and along with it the material's properties. Grain boundaries are among the most important defects in metals. Their energy, composition, and distribution directly affect the flow of dislocations and influence the thermodynamics of second phase and precipitate formation.

In alloys, segregation of solute atoms can alter grain boundary energy [1–3]. The effect of segregation can also manifest itself in other ways. Two other properties strongly affected by solute segregation are solute drag [2,4,5] and grain boundary wetting [2,6–8]. In the former case, the grain boundary energy is reduced by solute segregation, thus reducing the driving force to reduce surface area (excess free energy) of a grain boundary. In the latter case, solute segregation can dramatically affect the thermodynamics of grain boundary formation; not only can segregation alter at what undercooling grain boundary wetting occurs, but it can allow for different grain boundary states (e.g., grain boundary widths) [7].

There have been a number of experimental studies of grain boundary energy involving pure materials [9–11] and alloys [1,11]. Many studies have focused on characterization of solute segregation and distribution [2,3] as solute segregation typically has an important effect on grain boundary energy as demonstrated in [1,12,13]. For pure materials and dilute alloys, many of these studies have found that the grain boundary energy is well-fit by the well-known Read–Shockley Law when neighboring grains are misoriented by small angles [9,11]. It is also possible to adjust the parameters of the Read–Shockley equation to fit a larger range of misorientation angles [9–11].

A number of theoretical approaches have also been used to study grain boundary energy in metals. The most prevalent, for both pure materials and alloyed metals, are the analytic and semi-analytic dislocation models of Read and Shockley [11,14] and Van der Merwe [2], and models employing simple thermodynamic considerations of an interface [2,12]. Various computational approaches have also been employed to determine grain boundary energy in pure metals, including Monte Carlo simulations [15] and lattice statics [16]. Some computational approaches have also been used to model solutal effects in grain boundaries. These include monte carlo methods [3], molecular dynamics [3,13] and phase field simulations [7].

A relatively new continuum approach for modelling the effect of defects in non-equilibrium phase transitions has emerged in the past ten years known as the phase field crystal (PFC) method. The PFC methods have been developed as part of a continued

* Corresponding author. Tel.: +1 9059733520.
E-mail addresses: stollejf@mcmaster.ca (J. Stolle), provatas@physics.mcgill.ca (N. Provatas).

0927-0256/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.commatsci.2013.09.002

attempt to bridge the divide between traditional phase field modelling and molecular dynamics approaches [17]. In particular, PFC methods access diffusional time scales while incorporating the salient features of atomic-scale elasticity, plasticity [18–20] and dislocation properties [21]. In pure materials, PFC simulations of grain boundary energy have yielded excellent correspondence with the Read–Shockley theory of grain boundary energy versus misorientation [22,23]. They have also shed light on the physics of grain boundary pre-melting in pure materials [23,24]. To date, the grain boundary energetics in alloys simulated by PFC models has not been characterized.

This work systematically characterizes the thermodynamics of grain boundary segregation and grain boundary energy in two binary alloy PFC models, the first the original PFC model of Ref. [18] and the structural PFC model of Ref. [25]. Section 2 introduces the two PFC models used in this study and Section 3 reviews the Gibbs adsorption theorem. Section 4 reports on numerical simulations of the aforementioned PFC models that characterize grain boundary energy and compares computed solute adsorption to the prediction of Gibbs adsorption theorem. Our results are discussed in the context of previous experiments and theories. Section 5 discusses the effect of different model parameters on our results. Section 6 concludes and summarizes our study.

2. Phase field crystal models of a binary alloy

2.1. Original binary PFC model

The original phase field crystal model (PFC) of alloys characterized in this work is derived in detail in Ref. [18]. The resultant PFC free energy is expressed in terms of a temporally coarse-grained normalized crystal density field and a relative density difference that is analogous to a solute concentration field. In particular, the normalized total density is given by $n = (\rho - \rho_l)/\rho_l$ and the normalized concentration by $\psi = (\rho_1 - \rho_2)/\rho_l$, where the total density ρ is the sum of the density of each species, $\rho = \rho_1 + \rho_2$, and ρ_l is the density of a reference liquid state. The dimensionless Helmholtz free energy functional expressed in these variables is given by

$$F = \int_V \left\{ (B_0^L + B_2^L\psi^2)\frac{n^2}{2} + B^X n(2\nabla^2 + \nabla^4)\frac{n}{2} - t\frac{n^3}{3} + v\frac{n^4}{4} + w\frac{\psi^2}{2} + u\frac{\psi^4}{4} + K\frac{|\nabla\psi|^2}{2} + 2\eta B^X n\psi(\nabla^2 + \nabla^4)n\,d\vec{r} \right\} \quad (1)$$

where B_0^L is the isothermal compressibility of the liquid at $\psi = 0$, B_2^L determines how the isothermal compressibility of the liquid changes with ψ, B^X is related to elastic constants in the solid, and t, v, u are determined by the low order terms of a local expansion of the classical density functional theory description of the material, w is related to the atomic bond energies, and K is related to w and the lattice spacing [18]. The difference $B_0^L - B^X$ plays the role of normalized temperature variable. All lengths are scaled such that the lattice constant is $a = 4\pi/\sqrt{3}$ when the lattice mismatch parameter $\eta = 0$. The lattice spacing changes with concentration according to the parameter $\eta = (1/a)\partial a/\partial\psi$.

Assuming conserved dissipative dynamics for both fields, the evolution equations are:

$$\frac{\partial n}{\partial t} = \nabla^2\left(\frac{\delta F}{\delta n}\right) = \nabla^2\mu_n \quad (2)$$

$$\frac{\partial \psi}{\partial t} = \nabla^2\left(\frac{\delta F}{\delta \psi}\right) = \nabla^2\mu_\psi \quad (3)$$

In Eqs. (2) and (3), the constant atomic mobilities have been absorbed in the time variable and a noise term reflecting the effect of thermal fluctuations on the evolution of the system has been neglected. The local chemical potentials corresponding to each conserved field are given by $\mu_n = \delta F/\delta n$ and $\mu_\psi = \delta F/\delta\psi$.

Because we are solely analyzing thermodynamic aspects of the system, the equilibrium states can be found more quickly and accurately by solving:

$$\frac{\partial n}{\partial t} = -\left(\frac{\delta F}{\delta n} - \tilde{\mu}_n\right) \quad (4)$$

$$\frac{\partial \psi}{\partial t} = -\left(\frac{\delta F}{\delta \psi} - \tilde{\mu}_\psi\right) \quad (5)$$

where the macroscopic reservoir chemical potentials, $\tilde{\mu}_\psi$ and $\tilde{\mu}_n$, are thermodynamic control parameters, analogous to temperature and pressure, and t is pseudotime; this formalism is used for a pure material in Ref. [23].

Eqs. (1)–(3) can be represented on mesoscales by a set of complex order parameter equations, the coefficients of which are directly linked to those of the above PFC model, which is, in turn, linked to a simplified classical density functional theory of freezing. The complex order parameter representation of Eqs. (1)–(3) has also been shown to reduce to the form of a traditional scalar phase field model with coupled strain effects [17]. To the accuracy of a single-mode approximation, such an analysis thus yields a microscopic connection between continuum elastic effects and solute concentration and temperature.

2.2. Binary XPFC model

The second phase field crystal (PFC) model of binary alloys characterized in this work is derived in detail in Ref. [25]. The resultant PFC free energy is expressed in terms of a temporally coarse-grained normalized crystal density field and a solute concentration field. In particular, the normalized total density is given by $n = (\rho - \rho_0)/\rho_0$ and the concentration field by $c = \rho_2/(\rho_1 + \rho_2)$, where the total density ρ is the sum of the density of each species, $\rho = \rho_1 + \rho_2$, and ρ_0 is the density of a reference state. The dimensionless Helmholtz free energy functional expressed in these variables is given by

$$F = \int_V \left\{ \frac{n^2}{2} - \eta\frac{n^3}{6} + \chi\frac{n^4}{12} + \omega(c\ln(c/c_0) + (1-c)\ln((1-c)/(1-c_0))) - \frac{n}{2}\int_{V'}(C_{eff}(\vec{r}-\vec{r}')n(\vec{r}')d\vec{r}') + \alpha\frac{|\nabla c|^2}{2}\,d\vec{r} \right\} \quad (6)$$

where η and χ are prefactors chosen to fit the ideal free energy, ω and c_0 determines the strength of the entropy of mixing, and α is a constant related to the two-point correlation functions but taken here as a constant [25]. The correlation function, C_{eff}, is given by

$$C_{eff} = g(c)C_{11} + (1 - g(c))C_{22},$$
$$g(c) = 1 - \lambda c + (3 + \lambda)c^2 + 4$$

with λ being the enthalpy of mixing in the solid state and C_{xy} is the correlation function between species x and y. The fourier transform of this correlation function is given by:

$$\widehat{C}_{xx}(k) = \sum_{i=1}^{N} P_i \exp\left(-D_i\sigma^2 k_i^2\right)\exp\left(-G_i(k-k_i)^2\right)$$

where N is the total number of family of peaks, σ is a variable representing the temperature, k_i is the magnitude of the wave number of the family of peaks, D_i, P_i, and G_i are free parameters for the i^{th} family of planes, treated here for simplicity as adjustable constants. Note that the lattice spacing for each set of planes is $a_i = 2\pi/k_i$.

Assuming conserved dissipative dynamics for both fields, the evolution equations are: