Full length article

Thermodynamic properties of phase-field models for grain boundary segregation

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ABSTRACT

Impurity atoms segregated in grain boundary (GB) regions can dramatically change the physical and chemical properties of the GBs. Such changes often appear to be attributed to the GB energy reduction and/or solute drag effect. Phase-field models have been utilized to clarify both the thermodynamic and kinetic effects of the GB segregation. In this study, we developed phase-field models for GB segregation that are diffuse interface versions of the classical two-phase model of GB segregation. The thermodynamic state at any point in the system is represented as a mixture of a GB phase and a matrix phase. There are two choices for the thermodynamic relation between the GB phase and the matrix phase that constitute the point: the equal composition condition in model I and the equal diffusion potential condition in model II. Most of the previous PFMs for GB segregation appear to be specific cases of model I. We examined the thermodynamic properties of models I and II, and compared them with each other and the classical two-phase model. Although all the models resulted in the same GB composition, the GB energy and its dependency on the composition at the equilibrium state are quite different from each other. In model I, there is a lower bound to the GB energy, which originates from the equal composition condition. The GB energy from model II shows no such lower bound, and it is represented as the vertical distance between the parallel tangent lines on the free energy diagram, as in the classical two-phase model. Nevertheless, the compositional dependence in the model II is quite different from that in the classical two-phase model. This originates from the different choices for the composition-independent parameter in the models: a constant gradient energy coefficient in model II and a constant GB width in the classical two-phase model. Model I is not suitable for simulations of alloys that show a reduction of the GB energy due to GB segregation below a certain limit (in dilute alloys, about half of the GB energy of pure solvents). Model II is a correct choice for such alloys.

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1. Introduction

Solute atoms often segregate at the grain boundary (GB) region. Even impurities that are hardly detectable in the grain interior region (matrix) can be segregated at the GB region to very high concentrations. This GB segregation can fundamentally alter not only the microscopic GB dynamic [1], but also the macroscopic properties of the materials [2]. A typical example is the extraordinary thermal stability observed in many nanocrystalline materials. In nanocrystalline materials that show high resistance against grain growth, distinct GB segregation has often been observed [3—13]. The solute drag effect on GB motion and/or GB energy reduction due to the GB segregation has been claimed to be one of the causes of the retarded grain growth [9—19]. However, the key mechanism underlying the phenomenon seems to be far from a complete understanding [20—22].

The GB energy reduction, which is a thermodynamic aspect of GB segregation, has been studied using two different methods: the sharp interface and two-phase approaches. In the former approach [1,15—19], which is based on the Gibbs formalism of interface thermodynamics, the GB is regarded as a sharp interface with no finite thickness. In the latter approach [1,23—26], which we call the 'classical two-phase model' hereafter, the GB is regarded as a phase with a finite and constant thickness, and bulk thermodynamics is

applied to find the equilibrium state in the two-phase system of the matrix and GB phases. The study of the solute drag effect, which is a kinetic aspect of GB segregation, also has a long history, starting from Lücke and Detert [27] and Cahn [28]. The diffusional interaction between the moving GBs and the solute atoms to catch up with them gives rise to the drag force on moving GBs. If the solute segregation potential in the GB region and the free energy of the matrix phase are given, the drag force can be found by solving the diffusion equation [1,27—30].

Until late in the 20th century, the thermodynamic and kinetic aspects of GB segregation have been studied quite independently from each other. To correctly understand the thermal behaviors of the materials accompanying GB segregation, however, both aspects of GB segregation must be formulated in a unified way. One such unified approach is the phase-field model (PFM). PFMs [31—36], which were originally developed to simulate the diffusional phase transformation, are composed of two equations: the phase-field and diffusion equations. These two equations govern not only the thermodynamic properties of the system, but also the interaction between the moving interface and the diffusional field. Thus, PFMs for GB migration and grain growth have been developed to include both the thermodynamic and kinetic aspects of the segregation [37—45]. All the PFMs developed for GB segregation have a common ground that the free energy of the system is designed to be decreased for spontaneous segregation. In the details of the models, however, two different approaches have been adopted. In one approach [38—45], which has been employed in most PFMs for GB segregation, the system is assumed to be a single phase in the chemical aspect, but all the grains in the system are regarded as different phases from each other in the crystallographic orientation aspect. In the other approach, which was first developed by Cha et al. [37], the system is assumed to be composed of two phases (matrix phase and GB phase) with different compositions from each other. The GB phase fraction is unity at the center of the GB region, and it changes monotonously from one to zero in the matrix region.

The thermodynamic and kinetic properties of GBs have been examined for both approaches under the assumptions of ideal [40—42], dilute [37] or regular solutions [44]. However, there has not been any detailed examination of the differences in basic properties between the different approaches. In this study, we first develop a generalized two-phase PFM, which is the diffuse interface version of the classical two-phase model of GB segregation. We show that the previous models are specific cases of the two-phase PFM. We then compare the thermodynamic properties of the phase-field models and the classical two-phase model, and clarify where the differences between models come from. The kinetic properties of the models, such as the solute drag force, are also very important. However, even the equilibrium properties show nontrivial behaviors, depending on the models. In this study, therefore, we focus on the equilibrium properties of the models.

This work is organized as follows. In section 2, we briefly review the key concept of the classical two-phase thermodynamic model for GB segregation because it is closely related to the PFMs in this study. In section 3, we formulate a generalized PFM for GB segregation, and models I and II are derived by putting an additional condition on the thermodynamic state for an arbitrary infinitesimal point in the GB region. The GB energy and GB width are obtained for the arbitrary free energy densities of the matrix and GB phases, and the fundamental differences in GB energy among the phase-field models and the classical two-phase model are clarified. In section 4, we explicitly show the differences in the thermodynamic behaviors for specific forms of the free energy density. In the last section 5, we present the parameter fitting for the mesoscale simulation of grain growth with segregation and discuss the segregation induced recrystallization.

If necessary to keep consistency in presentation, we will rederive some of the relevant equations in several parts, but usually in simpler ways than in previous studies [37,41,42,44].

2. Classical two-phase model of GB segregation

As shown later, all of the PFMs for GB segregation can be regarded as two-phase models. Therefore, the classical two-phase model [1,23—26] for GB segregation should have close relationships with the PFMs for GB segregation. To clarify this point, we first briefly review the key concept of the classical two-phase model, following Hillert's approach [24]. In the classical model, the GB layer is regarded as a homogeneous volumetric phase with a constant width 2ξ, belonging to a separate phase from the matrix phase. It is assumed that the GB width is not a thermodynamic variable in a given alloy, but rather a fixed a priori value independent of the solute concentration in the alloy, and the GB energy corresponds to the free energy difference between the GB and matrix phases per unit GB area. If the free energies *per unit volume* of the GB and matrix phases for the pure A element are given as f_A^g and f_A^m, respectively, the GB energy σ_A is given by the free energy change when the matrix phase in a volume with a unit area and a width 2ξ is transformed into the GB phase with the same volume:

$$\sigma_A = 2\xi\left(f_A^g - f_A^m\right) \equiv 2\xi\omega_A, \tag{1}$$

where we defined

$$\omega_A = f_A^g - f_A^m, \tag{2}$$

because this parameter appears frequently throughout this study.

For an alloy at an equilibrium state, the composition of the GB phase and the GB energy change as a function of the matrix composition can be determined as follows. Let us consider a closed system of substitutional A-B alloy that is composed of two grains (matrix phase) and a GB phase with a width 2ξ between them. When this system is in an equilibrium state, the total free energy of the system is minimized. Equivalently, in the equilibrium state, all the driving forces for the chemical diffusion and the boundary migration between the matrix and GB phase should vanish. In the present system, the driving force for the phase boundary migration is irrelevant because the width 2ξ was assumed to be a fixed value. Thus, the equilibrium state is determined by the vanishing driving force for diffusion only. The driving force of the substitutional diffusion is the gradient of the diffusion potential $\tilde{\mu}$. Here, $\tilde{\mu} \equiv \mu_B - \mu_A$ is the difference between the chemical potential μ_B of the solute and μ_A of the solvent. This diffusion potential in phase p is equivalent to the slope df^p/du of the tangent line on the diagram of the free energy (f^p) curve as a function of the solute concentration u. Thus, the equilibrium condition for the present system is a constant diffusion potential over the whole space of the system, which results in the same diffusion potential in the matrix phase and GB phase. This can be graphically represented by a parallel tangent construction on the free energy-concentration diagram, as shown in Fig. 1. In this figure, f^m and f^g are the free energy densities of the matrix and GB phases, respectively. u_m and u_g are the solute compositions of the matrix and GB phases, respectively. The superscript e on the concentrations denotes the equilibrium concentration. The slope of the two parallel tangent lines (dotted lines) is the equilibrium diffusion potential

$$\tilde{\mu}^e \equiv \frac{df^m\left(u_m^e\right)}{du} = \frac{df^g\left(u_g^e\right)}{du}. \tag{3}$$