Layering transitions at grain boundaries

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ABSTRACT

We review various simplified models that have been advanced to describe layering (complexion) transitions at grain boundaries in multicomponent solids. In particular, we first outline lattice-gas, off-lattice atomistic and thermodynamic models that have been employed to investigate phase-like behavior at segregated grain boundaries. The results of these investigations are summarized in the form of complexion diagrams in different thermodynamic planes, and we highlight important features of these diagrams, such as complexion transition lines and critical points. Finally, we describe current issues and provide a future outlook.

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1. Introduction

In recent years there has been growing recognition of the importance of the role of structural and chemical transitions associated grain boundaries [1,2,4,5] in determining material properties. More specifically, observations of interface-stabilized "phases", known as complexions [6–8], have prompted investigations that have connected complexion transitions to changes in observed properties [9], including grain-boundary (GB) mobility and sintering behavior [10,11]. These investigations suggest that the ability to control complexion transitions may enable the tailoring of material properties via interfacial engineering. Given this intriguing possibility, it is necessary to understand the thermodynamics of such transitions in greater detail.

There are several approaches to modeling complexion transitions that underline the competing factors that dictate interfacial structure and chemistry. For example, Rickman et al. [12] generalized the lattice-gas model of surface adsorption of de Oliveira and Griffiths [13] to examine layering transitions at both low-and high-angle grain boundaries. This study highlighted the existence of complexion equilibria and associated transitions, as first observed in a regular-solution model by Wynblatt and Chatain [14,15]. In addition, Luo and coworkers employed a phenomenological, thermodynamic model [16–18] to identify GB complexions and developed associated diagrams that summarize regimes of complexion stability. This sharp-interface approach has been used to study complexions in multicomponent systems. We also note that Tang et al. [2] employed a phase-field model to examine complexion

transitions and their relative stability while Mishin et al. [3] used a similar model to study grain-boundary premelting in alloys. Finally, Frolov et al. [19] used molecular dynamics simulation of Ag diffusion in bicrystalline Cu to study structural phase transformations at grain boundaries.

In this article, we compare and contrast various simplified models that have been advanced to describe complexion transitions at grain boundaries in multicomponent solids. Our aim is to demonstrate that these models capture much of the essential physics associated with such transitions. After outlining several complexion models and summarizing a few relevant results, we briefly describe the diagrams that highlight regimes of stability and examine how these regimes may be altered as a function of, for example, temperature and stress. Finally, we address some of the outstanding issues in characterizing complexion transitions and in assessing their impact on material properties.

2. Models and methodology

Several complementary models have been proposed to describe the structure and chemistry associated with layering transitions at grain boundaries. We begin with a review of a binary, lattice-gas model in which the elastic interactions between atoms and a boundary are captured using results from the micromechanics of defects [12]. This approach is then extended to an off-lattice, atomistic model that embodies changes in boundary structure and vibrational modes that attend segregation [20]. A thermodynamic model that has been used to determine the stability of premelting-like, intergranular films is then discussed and compared with the other approaches for complexion modeling [16–18].

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2.1. Lattice-gas model

In this first approach, a grain boundary in a binary alloy is modeled using a modified lattice-gas Hamiltonian that reflects both the chemical and elastic interactions inherent in this system. For this purpose, our starting point is a Hamiltonian developed to study surface gas adsorption [13]. This modified, Ising-like Hamiltonian is given by

$$H = -J \sum_{\langle ijk; \, i'j'k' \rangle} n_{ijk} n_{i'j'k'} + \sum_{ijk} V_{ijk} n_{ijk}, \tag{1}$$

where J is an energy parameter, V_{ijk} is an external field, the angle brackets denote a nearest-neighbor summation and n_{ijk} is an occupancy variable equal to zero (one) if a given site is occupied by an A (B) atom. In a regular-solution model, J can be related to the interaction energies $\epsilon_{\alpha\beta}$ between atoms of type α and β. One finds that $J = (\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB})$.

We next extend this model to describe grain-boundary segregation in a bicrystal and associated complexion transitions [12]. In particular, we construct a mean-field grand potential, $\Omega(T, \Delta\mu)$, for a system in contact with a thermal reservoir having a temperature T and with a difference in chemical potential $\Delta\mu$ that reflects the aforementioned lattice-gas energetics. For simplicity, it is assumed that the configurational entropy is given by the ideal entropy of mixing. In this formulation V_{jk} embodies the elastic interactions between the lattice-gas atoms and the grain boundary. The equilibrium state of this system can then be determined by minimizing Ω with respect to the site-occupancy variables.

For the purposes of illustration, two limiting cases for V_{jk} are considered, namely those corresponding to generic low- and high-angle boundaries. In the former case, a low-angle tilt boundary is modeled as an array of edge dislocations [21,22] while, in the latter case, the boundary is regarded as an isotropic slab inhomogeneity that differs elastically from the surrounding medium [23]. In each case the atoms are modeled as spherical centers of dilatation in an (infinite) elastically isotropic medium. For simplicity, symmetric boundaries are employed here, and so only even numbers of segregated layers can be observed. In Section 3, we present complexion diagrams obtained from this analysis that illustrate coexistence between different interfacial states.

2.2. Binary Lennard-Jones system in the semi-grand canonical ensemble

Consider next a binary, atomistic model comprising lattice (A) atoms and impurity (B) atoms that incorporates off-lattice atomic motion and elastic interactions and permits one to vary the relevant intensive parameters, such as the temperature (T), the stress and the difference in chemical potential ($\Delta\mu$) [20]. For simplicity, a modified Lennard-Jones potential [24] having parameters ϵ_{ij} and σ_{ij} (where the subscripts denote atom type), with Lorentz-Berthelot rules [25] used to describe A-B interactions, is employed to capture the energetics of this system. As is customary, energy and length scales are reported in units of ϵ_{AA} and σ_{AA}, respectively. For a periodic simulation cell containing a grain boundary and a choice of interaction parameters, the system is equilibrated for a given T, stress component p_{zz} (where the z-direction in normal to the GB plane) and $\Delta\mu$ in the semi-grand canonical ensemble [26,27].

To study complexion transitions, it is useful to determine the ensemble-average interfacial excess $\Gamma = N_B/N_B^0$ at each boundary, where N_B is the number of B atoms within 3 lattice parameters of a grain boundary and N_B^0 is the maximum number of B atoms in the GB region, as a function of the intensive variables. The calculation of Γ enables the construction of a complexion diagram that

highlights complexion coexistence. In practice, this construction is accomplished by recording the fraction of simulation time associated with each value of Γ. From this information, one can then compile a histogram that reflects the associated probability distribution of Γ. This histogram is used, in turn, to plot the associated complexion miscibility gap and, in addition, to obtain the interfacial free energy of coexisting complexions. Some examples of this methodology are discussed in Section 3 below.

2.3. Thermodynamic model

At longer length scales, one can formulate a thermodynamic model of complexion equilibria in alloys by extending existing, sharp-interface models of premelting in single-component systems [28]. In this formulation, the excess GB energy of a (subsolidus) liquidlike intergranular film in an A-B alloy, relative the corresponding bulk phases, can be written as [18,29]

$$\sigma^x(h) = 2\gamma_{cl} + \Delta G_{amorph}^{(vol)} h + \sigma_{interfacial}(h), \tag{2}$$

where h is the effective interfacial width (commonly known as the film thickness), γ_{cl} is the energy of the crystal-liquid interface and $G_{amorph}^{(vol)}$ is the free-energy cost for forming an undercooled liquid [17]. The interfacial potential, $\sigma_{interfacial}(h)$, includes the effects of all interfacial interactions [18,29,30]. A stable subsolidus, liquidlike interfacial complexion may exist with a maximum interfacial width of

$$h < -\frac{\Delta\gamma}{G_{amorph}^{(vol)}} f(h), \tag{3}$$

where $\Delta\gamma = 2\gamma_{cl} - \sigma^x(h = 0)$ and the dimensionless interface coefficient, $f(h)$, is defined by

$$\sigma_{interfacial}(h) = -\Delta\gamma(1 - f(h)), \tag{4}$$

with the boundary conditions $f(h = 0) = 0$ and $f(h = +\infty) = 1$. From these considerations, it is convenient to define a parameter, λ, that scales the actual interface width as [31]

$$\lambda = -\frac{\Delta\gamma}{G_{amorph}^{(vol)}}. \tag{5}$$

The values of λ can be obtained for specific systems by estimating the relevant interfacial energies using statistical models and by employing bulk phase diagram (e.g., CALPHAD) data and tools. Computed λ values can then be plotted on bulk phase diagrams to construct "GB λ-diagrams", as in several previous studies [11,17,18,29,32]. We note that these diagrams are not rigorous GB complexion diagrams; however, they have been proven useful for forecasting trends in high-temperature GB disordering, activated sintering, Coble creep and other GB-controlled phenomena.

Eq. (2) can also be rewritten in dimensionless form as

$$\frac{\sigma^x(h) - \sigma^x(0)}{-\Delta\gamma} = -f(h) + \frac{h}{\lambda}. \tag{6}$$

The minimization of Eq. (6) with respect to h yields an equilibrium interfacial width, h_{eq}. If the interface coefficient decays exponentially with a characteristic length ξ (i.e., if $f(h) = 1 - \exp(-h/\xi)$) for metals having one dominant short-range interaction, a non-intrinsic GB complexion starts to develop ($h_{eq} > 0$) when $\lambda > \xi$, with an equilibrium interfacial width $h_{eq} = \xi \ln(\lambda/\xi)$. However, the interface coefficient for most real materials can be much more complex and difficult to quantify. More specifically, oscillatory interface coefficients (resulting from discrete atomic sizes) can produce layering transitions. Some examples will be presented in the next section.