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A differential cluster variation method for analysis of spinodal decomposition in alloys

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Abstract. A differential cluster variation method (DCVM) is proposed for analysis of spinoidal decomposition in alloys. In this method, lattice symmetry operations in the presence of an infinitesimal composition gradient are utilized to deduce the connection equations for the correlation functions and to reduce the number of independent variables in the cluster variation analysis. Application of the method is made to calculate the gradient energy coefficient in the Cahn-Hilliard free energy function and the fastest growing wavelength for spinodal decomposition in Al-Li alloys. It is shown that the gradient coefficient of congruently ordered Al-Li alloys is much larger than that of the disordered system. In such an alloy system, the calculated fastest growing wavelength is approximately 10 nm, which is an order of magnitude larger than the experimentally observed domain size. This may provide a theoretical explanation why spinodal decomposition after a congruent ordering is dominated by the antiphase boundaries.

PACS. 64.75.+g Solubility, segregation, and mixing; phase separation – 81.30.-t Phase diagrams and microstructures developed by solidification and solid-solid phase transformations – 05.70.Ln Nonequilibrium and irreversible thermodynamics

1 Introduction

Phase transformation is critically important to the development of new materials since it yields abundant microstructures in the micro/mesoscopic scales. For the spinodal decomposition, the phase transformation is determined mainly by diffusion since there is no thermodynamic barrier [1–3]. Compared with that in a nucleation process, the domain size distribution width in a spinodal decomposition of binary systems is greatly compressed, which may produce rather interesting nanostructures [4]. Spinodal decomposition has been commonly used to control grain structure in materials such as Alnico alloys and Al-Li alloys to enhance the properties of these materials [5–7].

The most widely used continuum theory to describe spinodal decomposition was presented by Cahn and Hilliard [8,9]. The free energy of a compositionally non-uniform alloy is expressed in the theory as a Ginzburg-Landau expression:

$$F\left(\{c(\mathbf{r})\}\right) = \int \left[f_0(c) + \kappa(\nabla c)^2\right] d^3\mathbf{r}, \tag{1}$$

where $f_0(c)$ is the local free energy density of the homogeneous system and κ is the gradient energy coefficient. In the initial stage of spinodal decomposition, the Cahn-Hilliard equation can be approximately linearized and analytically solved. When possible strain effect is ignored, one finds a fastest growing wavelength [10]

$$\lambda_m = 4\pi\left[\kappa \Big/ \frac{\partial^2 f_0(c)}{\partial c^2}\right]^{1/2}. \tag{2}$$

It has been recognized that λ_m is an important quantity to characterize domain size distribution in the decomposition process, hence could be useful in the design and evaluation of new materials. The local free energy density $f_0(c)$, which describes the equilibrium thermal properties of system, can be obtained from the highly accurate calculation-of-phase-diagram (CALPHAD) method or other theoretical methods such as cluster variation method (CVM) and molecular dynamics (MD). However, the gradient energy coefficient κ, as a parameter related to the non-equilibrium kinetics, has seldom been directly calculated. Considering only the nearest-neighbor interactions, κ of an AB binary alloy with simple cubic lattice was expressed under a point mean-field approximation (regular solution model) as [8]:

$$\kappa = \frac{2}{3}h^M_{0.5}r_0^2, \tag{3}$$

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in which $h_{0.5}^{M}$ is the heat of mixing per unit volume at the composition $c = 0.5$ and r_0 is the nearest-neighbor distance. Recently, by using a supercell CVM approach, Asta and Hoyt calculated the gradient coefficient of Ag-Al alloys and revealed some behaviors of κ that are different from the prediction of the regular solution model [11]. As these authors pointed out, the values of κ may have been influenced by the choice of parameters in their method because of the effects of higher order terms in the gradient expansion of the free energy. In this paper, we present a differential cluster variation method (DCVM) based on the infinitesimal analysis to calculate the gradient energy coefficient. As will be shown, this method naturally avoids the influence of the higher order terms in free energy expansion.

In phase transformation, the decomposition process can be accompanied by an ordering process. Due to the long-range diffusion associated with decomposition and the short-range diffusion associated with ordering, a congruent ordering process frequently occurs prior to the decomposition process [12]. For example, in Al-Li alloys, an important aerospace material, ordering and decomposition processes result in precipitates of an ordered δ' (Al_3Li) phase. If an congruent ordering process takes place first, spinodal decomposition does not occur from an initial disordered phase, but from a congruent ordered phase, in which case equation (3) is no longer applicable. It would be interesting to explore the influence of congruent ordering on the values of κ. By using the proposed DCVM method, we will calculate the gradient coefficient and the fastest growing wavelength of Al-Li alloys, and discuss implications on the actual decomposition process.

2 Methods

Cluster variation method (CVM) is a highly efficient microscopic method to evaluate the configurational free energy and determine the order-disorder phase transformation [13–15]. In an alloy system, the configurational free energy is determined by the probabilities of all possible configurations. The essence of CVM lies in using the probability of some small clusters to approximately evaluate the probability of the entire system in order to greatly decrease the number of independent variables. To facilitate the calculation, lattice symmetry is used to reduce the number of independent variables. For the homogeneous alloys, the pair of integers (n, t) is always used when referring to a specific n-point cluster with index t [16]. In the general case of inhomogeneous systems, a site variable $\mathbf{r}$ is needed to specify the location of the cluster [11]. In this paper, we denote $\gamma \equiv (n, t)$, and thus $(\mathbf{r}, \gamma)$ to specify a cluster. Clusters $(\mathbf{r}, \gamma)$ and $(\mathbf{r}', \gamma)$ are related by a displacement translation $\mathbf{r}' - \mathbf{r}$. The correlation function of the cluster $(\mathbf{r}, \gamma)$ is denoted as $\xi_{\mathbf{r},\gamma}$. The equilibrium value of $\xi_{\mathbf{r},\gamma}$ is determined by macroscopic conditions such as alloy composition c and temperature T. For the system with translational symmetry, we have the following relation:

$$\xi_{\mathbf{r}+\mathbf{L},\gamma}(c) = \xi_{\mathbf{r},\gamma}(c), \tag{4}$$

where $\mathbf{L}$ is the displacement vector of the symmetry operation. (T is omitted in the equation since it is always a constant.) By using the above relation, the equilibrium properties of the homogeneous system, including the local free energy density $f_0(c)$ in equation (1), can be determined in the conventional CVM procedure.

When there are compositional fluctuations in the system, the free energy can be expanded with respect to the homogeneous state. In principle, the compositional fluctuations can be expressed as a sum of Fourier components and the free energy expansion of any Fourier component can be independently solved by the general $\mathbf{k}$-space formalism in standard fluctuation theories [17]. In this paper, however, we directly consider a composition gradient in the system to evaluate the gradient coefficient κ in equation (1). The introduction of a gradient usually destroys the lattice symmetry (point group and translations), and equation (4) is no longer valid. The number of independent variables would become much larger than that in the homogeneous case. (Correlation functions of all clusters related by the symmetry operations are equivalent and can be represented by the same independent variable.) One method to solve this problem is to enlarge the number of independent variables, i.e., to use a supercell, to include a non-uniform composition variance. In the work of Asta and Hoyt, 98 planes were used to calculate the gradient coefficient of Ag-Al alloys [11].

Here, we develop a differential cluster variation method to solve the problem. The method is based on the observation that equation (1) is defined under the condition of small composition gradient ∇c. If ∇c is too large, higher order terms in the free energy expansion may be important and can not be simply ignored. To avoid the influence of higher order terms, we examine the response of the system to an infinitesimal composition gradient. In such an analysis, clusters related by lattice symmetry operations under the uniform state can be related under an infinitesimal gradient variance. A supercell is thus unecessary.

In our method, two kinds of infinitesimal variances upon the system are considered: (1) an infinitesimal composition gradient $\nabla c = d\mathbf{g}$ which keeps the composition at the origin as c and (2) an infinitesimal uniform composition variance dc. The correlation function under such variances is denoted as $\xi_{\mathbf{r},\gamma}(c, d\mathbf{g}, dc)$ [the correlation function of the homogeneous system is $\xi_{\mathbf{r},\gamma}(c)$]. By applying the Taylor expansion,

$$\begin{aligned}\xi_{\mathbf{r},\gamma}(c, d\mathbf{g}, dc) = \xi_{\mathbf{r},\gamma}(c) + \left(\frac{\partial \xi_{\mathbf{r},\gamma}(c)}{\partial \mathbf{g}} \cdot d\mathbf{g} + \frac{\partial \xi_{\mathbf{r},\gamma}(c)}{\partial c} dc\right) \\ + \frac{1}{2}\left[\frac{\partial^2 \xi_{\mathbf{r},\gamma}(c)}{\partial \mathbf{g} \partial \mathbf{g}} : d\mathbf{g} d\mathbf{g} + 2\frac{\partial^2 \xi_{\mathbf{r},\gamma}(c)}{\partial \mathbf{g} \partial c} \cdot d\mathbf{g} dc \right. \\ \left. + \frac{\partial^2 \xi_{\mathbf{r},\gamma}(c)}{\partial c^2}(dc)^2\right],\end{aligned} \tag{5}$$

where $\frac{\partial \xi}{\partial \mathbf{g}}, \frac{\partial \xi}{\partial c}, \frac{\partial^2 \xi}{\partial \mathbf{g} \partial \mathbf{g}}, \ldots$ are expansion coefficients to be determined by minimizing the free energy. We have expanded ξ only to second order terms because the gradient

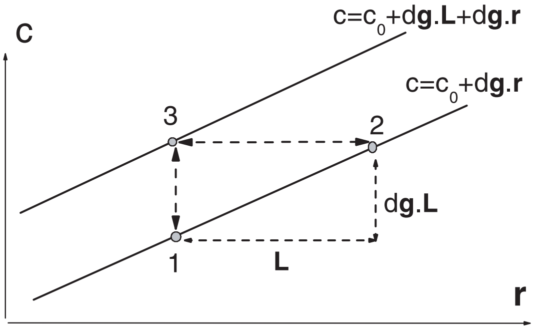

Fig. 1. Schematic graphics of the translation symmetry under a compositional gradient $d\mathbf{g}$. After the translation with a displacement $\mathbf{L}$, point 1 changes into point 2. If there is a uniform composition variance $\mathbf{L}\cdot d\mathbf{g}$, point 1 changes into point 3, which is equivalent to point 2.

energy in equation (1) is related to the second order terms of the free energy. Now consider a translation operation $\mathbf{L}$ which is a symmetry operation under the uniform case. When there is a gradient variance $d\mathbf{g}$, the system after the translation is not identical to that before the translation (see Fig. 1, point 1 is not equivalent to point 2). The composition of the system changed by $\mathbf{L}\cdot d\mathbf{g}$ after translation. Therefore, for two clusters located at $\mathbf{r}$ and $\mathbf{r}+\mathbf{L}$ which are related by the translation operation, the symmetry property gives

$$\xi_{\mathbf{r}+\mathbf{L},\gamma}(c, d\mathbf{g}, dc) = \xi_{\mathbf{r},\gamma}(c, d\mathbf{g}, dc + \mathbf{L}\cdot d\mathbf{g}). \tag{6}$$

(See Fig. 1, point 2 is equivalent to point 3.) Substituting equation (5) into the above equation yields

$$\begin{aligned}
&\xi_{\mathbf{r}+\mathbf{L},\gamma}(c) + \left(\frac{\partial \xi_{\mathbf{r}+\mathbf{L},\gamma}(c)}{\partial \mathbf{g}}\cdot d\mathbf{g} + \frac{\partial \xi_{\mathbf{r}+\mathbf{L},\gamma}(c)}{\partial c} dc\right)\\
&\quad + \frac{1}{2}\left[\frac{\partial^2 \xi_{\mathbf{r}+\mathbf{L},\gamma}(c)}{\partial \mathbf{g}\partial \mathbf{g}} : d\mathbf{g}d\mathbf{g} + 2\frac{\partial^2 \xi_{\mathbf{r}+\mathbf{L},\gamma}(c)}{\partial \mathbf{g}\partial c}\cdot d\mathbf{g}dc \right.\\
&\qquad\left. + \frac{\partial^2 \xi_{\mathbf{r}+\mathbf{L},\gamma}(c)}{\partial c^2}(dc)^2\right]\\
&= \xi_{\mathbf{r},\gamma}(c) + \left[\frac{\partial \xi_{\mathbf{r},\gamma}(c)}{\partial \mathbf{g}}\cdot d\mathbf{g} + \frac{\partial \xi_{\mathbf{r},\gamma}(c)}{\partial c}(dc + \mathbf{L}\cdot d\mathbf{g})\right]\\
&\quad + \frac{1}{2}\left[\frac{\partial^2 \xi_{\mathbf{r},\gamma}(c)}{\partial \mathbf{g}\partial \mathbf{g}} : d\mathbf{g}d\mathbf{g} + 2\frac{\partial^2 \xi_{\mathbf{r},\gamma}(c)}{\partial \mathbf{g}\partial c}\cdot d\mathbf{g}(dc + \mathbf{L}\cdot d\mathbf{g})\right.\\
&\qquad\left. + \frac{\partial^2 \xi_{\mathbf{r},\gamma}(c)}{\partial c^2}(dc + \mathbf{L}\cdot d\mathbf{g})^2\right],
\end{aligned} \tag{7}$$

which leads to the following connection equations for the expansion components:

$$\xi_{\mathbf{r}+\mathbf{L},\gamma}(c) = \xi_{\mathbf{r},\gamma}(c), \tag{8}$$

$$\frac{\partial \xi_{\mathbf{r}+\mathbf{L},\gamma}(c)}{\partial \mathbf{g}} = \frac{\partial \xi_{\mathbf{r},\gamma}(c)}{\partial \mathbf{g}} + \frac{\partial \xi_{\mathbf{r},\gamma}(c)}{\partial c}\mathbf{L}, \tag{9}$$

$$\frac{\partial \xi_{\mathbf{r}+\mathbf{L},\gamma}(c)}{\partial c} = \frac{\partial \xi_{\mathbf{r},\gamma}(c)}{\partial c}, \tag{10}$$

$$\frac{\partial^2 \xi_{\mathbf{r}+\mathbf{L},\gamma}(c)}{\partial \mathbf{g}\partial \mathbf{g}} = \frac{\partial^2 \xi_{\mathbf{r},\gamma}(c)}{\partial \mathbf{g}\partial \mathbf{g}} + 2\frac{\partial^2 \xi_{\mathbf{r},\gamma}(c)}{\partial \mathbf{g}\partial c}\mathbf{L} + \frac{\partial^2 \xi_{\mathbf{r},\gamma}(c)}{\partial c^2}\mathbf{L}\mathbf{L} \tag{11}$$

$$\cdots$$

For a point group operation, similar equations can also be derived in a similar way. Based on these equations, for a group of clusters related by the symmetry operations of the lattice, their correlation functions can be expressed by that of a representative independent cluster even if there is an infinitesimal gradient variance.

To deduce the equations to solve the expansion coefficients, we expand the differential of the free energy as:

$$\begin{aligned}
\frac{\partial F(c, d\mathbf{g}, dc)}{\partial \xi_{\mathbf{r},\gamma}} &= \frac{\partial F(c)}{\partial \xi_{\mathbf{r},\gamma}} + \sum_{\mathbf{r}',\gamma'} \frac{\partial^2 F(c)}{\partial \xi_{\mathbf{r},\gamma}\partial \xi_{\mathbf{r}',\gamma'}} d\xi_{\mathbf{r}',\gamma'}\\
&\quad + \frac{1}{2}\sum_{\mathbf{r}',\gamma';\mathbf{r}'',\gamma''} \frac{\partial^3 F(c)}{\partial \xi_{\mathbf{r},\gamma}\partial \xi_{\mathbf{r}',\gamma'}\partial \xi_{\mathbf{r}'',\gamma''}} d\xi_{\mathbf{r}',\gamma'} d\xi_{\mathbf{r}'',\gamma''}\\
&= \frac{\partial F(c)}{\partial \xi_{\mathbf{r},\gamma}} + \sum_{\mathbf{r}',\gamma'} \frac{\partial^2 F(c)}{\partial \xi_{\mathbf{r},\gamma}\partial \xi_{\mathbf{r}',\gamma'}} \left\{\left(\frac{\partial \xi_{\mathbf{r}',\gamma'}(c)}{\partial \mathbf{g}}\cdot d\mathbf{g} + \frac{\partial \xi_{\mathbf{r}',\gamma'}(c)}{\partial c} dc\right)\right.\\
&\quad + \frac{1}{2}\left[\frac{\partial^2 \xi_{\mathbf{r}',\gamma'}(c)}{\partial \mathbf{g}\partial \mathbf{g}} : d\mathbf{g}d\mathbf{g} + 2\frac{\partial^2 \xi_{\mathbf{r}',\gamma'}(c)}{\partial \mathbf{g}\partial c}\cdot d\mathbf{g}dc\right.\\
&\qquad\left.\left. + \frac{\partial^2 \xi_{\mathbf{r}',\gamma'}(c)}{\partial c^2}(dc)^2\right]\right\}\\
&\quad + \frac{1}{2}\sum_{\mathbf{r}',\gamma';\mathbf{r}'',\gamma''} \frac{\partial^3 F(c)}{\partial \xi_{\mathbf{r},\gamma}\partial \xi_{\mathbf{r}',\gamma'}\partial \xi_{\mathbf{r}'',\gamma''}}\\
&\quad \times \left(\frac{\partial \xi_{\mathbf{r}',\gamma'}(c)}{\partial \mathbf{g}}\cdot d\mathbf{g} + \frac{\partial \xi_{\mathbf{r}',\gamma'}(c)}{\partial c} dc\right)\\
&\quad \times \left(\frac{\partial \xi_{\mathbf{r}'',\gamma''}(c)}{\partial \mathbf{g}}\cdot d\mathbf{g} + \frac{\partial \xi_{\mathbf{r}'',\gamma''}(c)}{\partial c} dc\right).
\end{aligned} \tag{12}$$

For a non-point cluster $(\mathbf{r},\gamma)$, the minimization of the free energy gives

$$\frac{\partial F(c, d\mathbf{g}, dc)}{\partial \xi_{\mathbf{r},\gamma}} = 0. \tag{13}$$

For a point cluster $(\mathbf{r},\gamma)$, the free energy should be minimized under the composition constraint as

$$\frac{\partial F(c, d\mathbf{g}, dc)}{\partial \xi_{\mathbf{r},\gamma}} = \mu_{\mathbf{r}}, \tag{14}$$

where $\mu_{\mathbf{r}}$ is the chemical potential at site $\mathbf{r}$ which controls the composition in the system. It has a uniform value at different sites in a homogeneous system [15]. When there is a gradient composition variance, $\mu_{\mathbf{r}}$ also varies with the gradient. Combining equations (12–14) and utilizing equations (8−11), the equations to determine the expansion coefficients, $\frac{\partial \xi}{\partial \mathbf{g}}, \frac{\partial \xi}{\partial c}, \frac{\partial^2 \xi}{\partial \mathbf{g}\partial \mathbf{g}}, \ldots$, can be easily obtained.

After solving the expansion coefficients, one can calculate the free energy of the system under any infinitesimal gradient and uniform variances as:

$$F(c, d\mathbf{g}, dc) = F(c) + \sum_{\mathbf{r},\gamma} \frac{\partial F(c)}{\partial \xi_{\mathbf{r},\gamma}} d\xi_{\mathbf{r},\gamma} + \frac{1}{2} \sum_{\mathbf{r},\gamma;\mathbf{r}',\gamma'} \frac{\partial^2 F(c)}{\partial \xi_{\mathbf{r},\gamma} \partial \xi_{\mathbf{r};,\gamma'}} d\xi_{\mathbf{r},\gamma} d\xi_{\mathbf{r}',\gamma'}. \quad (15)$$

The gradient energy coefficient κ is then calculated according to equation (1). Since the free energy is expressed as an energy part and an entropy part in CVM, one can independently calculate the contributions of energy and entropy to the gradient coefficients. In the regular solution model, the entropy depends only on the point probability, hence has no contribution to the gradient coefficient [8]. When the correlations between different points are considered (such as CVM), as will be demonstrate next, the entropy will give a finite contribution to the value of κ.

The method proposed here can be generalized to including higher order terms in the expansion of the free energy and other kinds of infinitesimal variance. This will not be pursued in this paper.

3 Results and discussions

In this section, the method presented above is applied to calculate the gradient energy coefficient along the (100) direction in an fcc lattice.

To compare the new method with the regular solution approximation [8], we first consider an exemplary AB spinodal system with the nearest-neighbor interaction. The value of the nearest-neighbor effective pair interaction is arbitrarily chosen as $-100k_B$ (k_B is the Boltzmann constant). The nearest neighbor pair is used as the basic cluster in CVM calculation for this case. This is a very "pure" spinodal system that experiences a decomposition into a mixture of A-rich and B-rich disordered phases at low temperatures. There is no other ordering or decomposition process in the system. The spinodal temperature at a composition $c = 0.5$ is determined as $T_c = 1090$ K in our calculation.

In Figure 2 the calculated values of κ are plotted as a function of composition at temperatures $T = 500$ and 700 K. The result of the regular solution model is also plotted as the dotted line for comparison. The κ value at $c = 0.5$ is very close to the prediction of the regular solution model. When the composition deviates from 0.5, κ increases steadily. Such behaviors originate from the pair correlations that are ignored in the regular solution approximation. These characteristics are consistent with previous supercell CVM calculation results on Ag-Al alloys, where a similar spinodal decomposition process on disordered phase was considered [11]. In contrast to reference [11], no abnormal behavior is observed at $c = 0$ in Figure 2.

We turn to a more realistic system, Al-Li alloys, an example of material ordering strengthening [6,7,18]. In this system, the ordering process usually occurs much faster than the decomposing process due to the difference in diffusion length scales [19,20]. We first optimize the ordered parameter at every composition by the conventional CVM process, and then use the DCVM method to investigate the response of the system to a gradient variance. In other words, we calculate the gradient coefficient of the congruent ordered phase. The effective pair interaction parameters are taken from the study of Garland et al. [21], where the nearest and second-nearest-neighbor effective pair interactions were chosen as $210k_B$ and $-105k_B$, respectively.

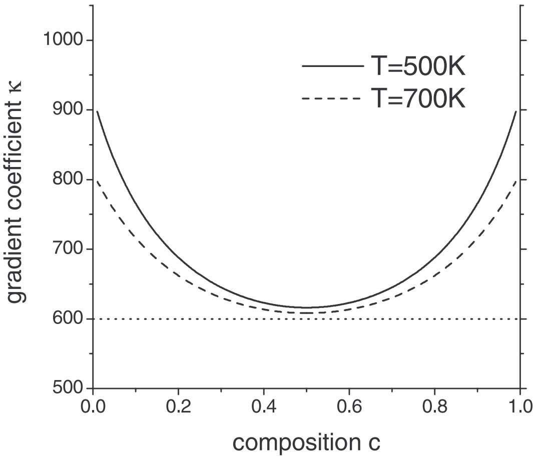

Fig. 2. The gradient energy coefficient κ (in units of k_B/r_0 where r_0 is the lattice constant) of a disordered fcc binary system as a function of the composition c. The dotted line denotes the prediction of the regular solution model.

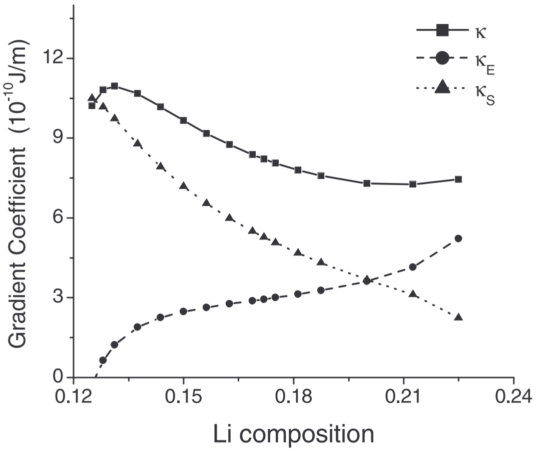

Fig. 3. The gradient coefficient (κ) with the corresponding contributions from energy (κ_E) and entropy (κ_S) of the congruent ordered Al-Li alloys as a function of the Li composition when the temperature is fixed at $T = 500$ K.

The calculated gradient energy coefficient κ, together with the contributions from energy and entropy parts (κ_E and κ_S), are shown in Figure 3 as functions of the Li composition at $T = 500$ K. An extraordinary characteristic of the result is that the calculated κ of Al-Li alloys here is about one order of magnitude larger than that in Ag-Al

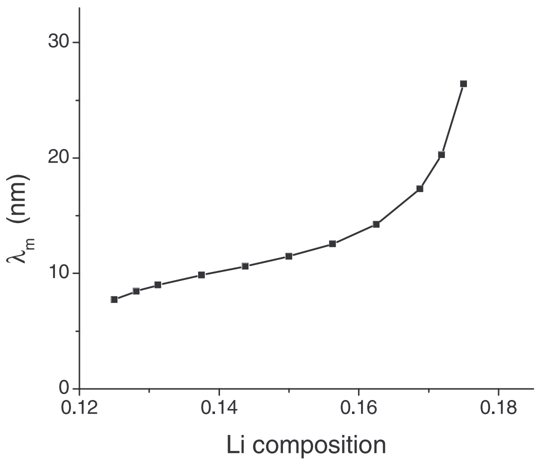

Fig. 4. The fastest growing wavelength λ_m of the congruent ordered Al-Li alloys calculated according to equation (2). The temperature is fixed at $T = 500$ K.

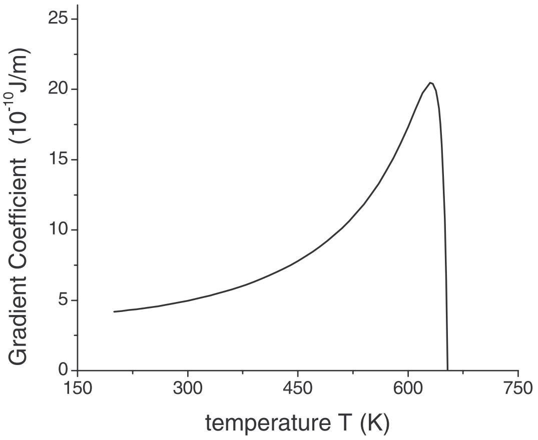

Fig. 5. The gradient coefficient of the congruent ordered Al-Li alloys as a function of temperature when the Li composition is fixed at 15%.

and Al-Zn alloys [11,22]. This indicates that the congruent ordering greatly affects the gradient coefficient of the system. When a congruent ordering occurs in Al-Li alloys, the face-center sites of the fcc lattice are mainly occupied by the Al atoms, resulting in a very low local Li composition at these sites. This may be an important source of the large κ in Al-Li alloys as κ increases at small compositions in an disordered phase (Fig. 2 and Ref. [11]).

By using the κ value in Figure 3, the fastest growing wavelength λ_m is calculated according to equation (2) for various Li compositions. It appears that λ_m is on the order of about 10 nm (Fig. 4). According to previous experiments and microscopic simulations, the modulation wavelength of Al-Li alloys in the early stage is about $1 \sim 2$ nm [23,24]. The discrepancy between the calculated λ_m value and the experiments and the pervious simulation results may be attributed to the existence of antiphase boundaries in the congruent ordered phase. When a spinodal decomposition occurs after a congruent ordering, the microscopic simulation reveals that the structural evolution in the decomposition process is dominated by the antiphase boundaries produced in the congruent ordering process, e.g., the equilibrium disordered phase appears and grows at the antiphase boundaries [12,19]. The antiphase boundaries play the role of nuclei for phase decomposition. Thus the modulation wavelength is determined by the distribution of antiphase boundaries. However, inside the spinodal region of the phase diagram, any fluctuation, no matter how small in degree, decreases the free energy and destablize the system. It is thus quite confusing why a spinodal decomposition does not occur spontaneously inside the congruent ordered domains even. The calculation result of the fastest growing wavelength in Figure 4 may provide an answer to this puzzle. For the spinodal decomposition process, there is a critical wavelength $\lambda_c = \lambda_m/\sqrt{2}$. Fourier components with modulation wavelength $\lambda < \lambda_c$ tend to decay while those with $\lambda > \lambda_c$ will grow. According to the results in Figure 4, the critical wavelength λ_c is larger than the size of congruent ordered domains observed in experiments and in previous simulations. Therefore, the spinodal process is suppressed inside the congruent ordered domains. On the basis of this explanation, when the decomposition process occurs after the congruent ordering, there is no essential difference for the systems inside and outside the spinodal region due to the antiphase boundaries.

In the work of Banerjee et al. [25], different instabilities in Al-Li alloys were determined using first-principles calculations in conjunction with the static concentration wave model, where the critical spinodal corresponds to the states with an infinite fastest growing wavelength [$\lambda_m \to \infty$ with $\partial^2 f_0(c)/\partial c^2 = 0$, see Eq. (2)]. Our above analysis suggests that the antiphase boundaries also play important role on the stability of the systems when the kinetic effect is involved.

It should be noted that the strain energy is not considered in the present calculation of the fastest growing wavelength λ_m. If the strain effect is involved, λ_m is expected to be larger than the current values, which will not change the above conclusions.

Figure 5 shows the gradient energy coefficient κ of Al-Li alloys as functions of temperature when the Li composition is fixed as 15%. κ of Al-Li alloys increases with increasing temperature. Only when the temperature is close to the stability limit of the ordered phase does the κ value drop rapidly.

4 Summaries

In this paper, a differential cluster variation method (DCVM) is developed and used to calculate the gradient energy coefficient (κ) in the Cahn-Hilliard course-grained free energy for spinodal decomposition. The symmetry equations of clusters are deduced from the symmetry operations of a lattice under an infinitesimal composition gradient in the system. This treatment significantly reduces the number of independent variables in comparison with a supercell CVM analysis. The DCVM is an intrinsic method to determine different order terms in the gradient expansion of the free energy. As example applications, the value of κ are calculated by this new method for two alloy systems with fcc lattice. It is shown that the κ values for systems with only the nearest-neighbor interaction are very close to the prediction of the point mean-field approximation (regular solution model), while significant differences emerge at low temperatures and extreme compositions. For the Al-Li alloys where a congruent ordering occurs prior to the spinodal decomposition, κ is found to be much larger than the disordered system. The fastest growing wavelength is calculated to be approximately 10 nm at 500 K, which is one order of magnitude larger than the experimentally observed domain size. This provides a theoretical explanation of the previous discovery that the spinodal decomposition after congruent ordering is dominated by antiphase boundaries produced in the congruent ordering process.

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