NON-CLASSICAL NUCLEATION THEORY OF ORDERED INTERMETALLIC PRECIPITATES—APPLICATION TO THE Al–Li ALLOY

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Abstract—The continuum non-classical nucleation theory of Cahn and Hilliard for isostructural decomposition has been extended to the case in which the precipitate and matrix not only have different compositions, but also have different structures. The particular example of precipitation of ordered intermetallics from a disordered matrix is considered. It is found that a critical nucleus consists of fluctuations of both composition and long-range order parameter profiles. It is shown that only when the composition of the initial disordered matrix is near the phase boundary of the disordered phase, are the composition and order parameter values inside the critical nucleus close to those of the equilibrium ordered phase, and that the critical profiles become increasingly diffuse as the composition of the disordered matrix approaches the ordering instability line. Based on the non-classical nucleation theory, the size of critical fluctuations, the critical free energy change and the nucleation rate are estimated for the specific case of the precipitation of metastable δ' ordered phase from a disordered matrix in the Al–Li alloy. Copyright © 1996 Acta Metallurgica Inc.

1. INTRODUCTION

Cahn and Hilliard [1] developed a continuum model taking into account the diffuse nature of interfaces, and studied the composition profiles of a critical nucleus, as a function of matrix composition from close to its equilibrium composition (c_x), to the spinodal composition (c_s) (see Fig. 1). They found that, for matrix compositions near c_x, the composition within a critical nucleus was almost identical to that of the equilibrium precipitate phase (c_β). As the matrix composition increases from c_x, the profiles of a critical nucleus became increasingly diffuse, with the composition within the nucleus approaching that of the matrix. Based on this study, they concluded that classical nucleation, which required the nucleus composition to be uniform and equal to c_β, was operative only when the matrix composition of the alloy was close to c_x. They also found that the radius of the critical nucleus diverged to infinity not only near c_x, as predicted by the classical nucleation theory, but also near c_β. More recently, LeGoues et al. [2] used a discrete lattice model [3] to calculate the profiles of the occupation probabilities (which refer to the probability that a given lattice site is occupied by an atom of a given type) for a critical nucleus, and found that at high temperatures and low supersaturations their profiles matched very well with those obtained using the Cahn–Hilliard continuum model. Only at intermediate compositions are there some differences between the profiles obtained from the continuum and discrete models. They found qualitative agreement with the continuum model for the variation of the radius of the critical nucleus with composition, as well. More details concerning the non-classical nucleation theory can be found in the review papers [4–6].

It should be emphasized that all previous works on non-classical nucleation, including the two mentioned in the previous paragraph, are concerned with isostructural decomposition. in which the precipitate phase and the matrix have the same structure and only differ in their compositions. However, in most of the important alloy systems, such as Ni–Al and Al–Li two-phase alloys, the precipitate phase is an ordered intermetallic and the matrix is a disordered phase, i.e. the precipitate and matrix not only have different compositions but also have different structures related by ordering. In these cases, a critical nucleus, or critical fluctuation, has to be characterized by both the composition and long-range order parameter profiles. Therefore, the main objective of this paper is to extend the original non-classical nucleation theory of Cahn and Hilliard for isostructural decomposition to the case in which the precipitate and matrix phases differ in both structures and compositions. We will apply the non-classical theory to a particular example, i.e. precipitation of the $L1_2$ ordered (Al_3Li) particles (δ') from an f.c.c. disordered matrix (α) in the Al–Li alloy system, in which the elastic energy contribution to nucleation can be ignored.

2. THE THEORY

In the original diffuse-interface theory of Cahn and Hilliard [1], the total free energy, F, of a system which is inhomogeneous in composition, c, is written as

$$F = \int [f(c) + (K_c/2)\nabla c)^2]d^3x \qquad (1)$$

where $f(c)$ is the local free energy density and K_c is the composition gradient energy coefficient. The increase in the free energy arising from a composition fluctuation in an alloy with average composition c_0, is then given by

$$\Delta F = \int [\Delta f(c) + (K_c/2)(\nabla c)^2]d^3x \qquad (2)$$

where

$$\Delta f = f(c) - f(c_0) - (c - c_0)(\partial f/\partial c)_{c_0}. \qquad (3)$$

If one assumes that nucleation in a metastable solution takes place by overcoming the minimum energy barrier, a critical nucleus is defined as the spatial composition fluctuation which has the minimum free energy increase among all fluctuations which lead to nucleation. If the interfacial energy is isotropic, the critical fluctuation is expected to have a spherical symmetry. In this particular case, the composition profile corresponding to the critical nucleus can be obtained by solving the following Euler equation in spherical coordinates,

$$K_c\frac{d^2c}{dr^2} + \frac{2K_c}{r}\frac{dc}{dr} = \frac{\partial \Delta f}{\partial c} \qquad (4)$$

subject to the boundary conditions,

$dc/dr = 0$ at $r=0$; $c = c_0$ and $dc/dr = 0$ at $r = \infty$.

The free energy increase corresponding to the critical fluctuation can then be obtained by substituting the solution from equation (4) into the spherical coordinates equivalent to equation (2).

However, the above theory is applicable only to the case in which a critical nucleus differs from the matrix only in composition. For precipitation of an ordered phase from a disordered matrix, we have to consider both the composition and structural differences between the nucleus and the matrix. Therefore, we have to consider the free energy functional as a function of both composition and long-range order parameter profiles. In this case, the increase in free energy, upon the formation of a fluctuation described by both composition and long-range order parameter profiles, is given by

$$\Delta f = \int [\Delta f + (K_\eta/2)(\nabla \eta)^2 + (K_c/2)(\nabla c)^2]d^3x \qquad (5)$$

where

$$\Delta f = f(\eta,c) - f(0,c_0) - (c - c_0)\left(\frac{\partial f}{\partial c}\right)_{0,c_0}. \qquad (6)$$

where f is the local free energy density which is a function of both composition and order parameter, c_0 is the average matrix composition, K_η and K_c are the gradient energy coefficients for order parameter and composition, respectively. Here η is the long-range order parameter, such that it varies from 0 for a completely disordered phase, to c for a completely ordered phase. Krzanowski and Allen [7] have used a similar scheme to calculate the interfacial energy of a flat anti-phase boundary between two ordered domains with solute segregation. If we assume that the system is isotropic and the critical nucleus has spherical symmetry, we can write equation (5) as

$$\Delta F = 4\pi \int [\Delta f + (K_\eta/2)(d\eta/dr)^2$$
$$+ (K_c/2)(dc/dr)^2]r^2dr. \qquad (7)$$

where r is the radial distance from the center of the fluctuation. The critical composition and order parameter profiles satisfy the Euler equations in spherical coordinates, given by

$$K_c\frac{d^2c}{dr^2} + \frac{2K_c}{r}\frac{dc}{dr} = \frac{\partial \Delta f}{\partial c}$$

$$K_\eta\frac{d^2\eta}{dr^2} + \frac{2K_\eta}{r}\frac{d\eta}{dr} = \frac{\partial \Delta f}{\partial \eta}. \qquad (8)$$

subject to the boundary conditions

$$c(r) = c_0 \quad \text{and} \quad \eta(r) = 0 \text{ at } r = \infty,$$

and

$$\frac{dc}{dr} \quad \text{and} \quad \frac{d\eta}{dr} = 0 \text{ at } r = 0.$$

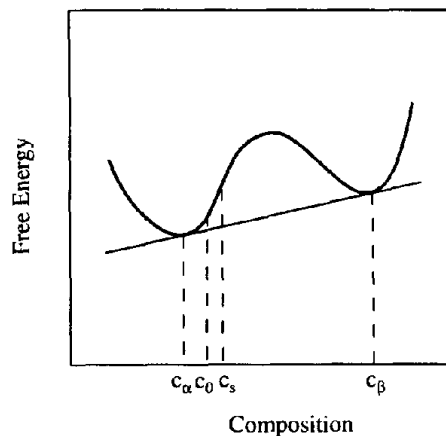These are coupled, non-linear second-order differen-

Fig. 1. Hypothetical free energy-composition curve for a system exhibiting isostructural decomposition.

tial equations. which have to be solved numerically for a given set of f, K_c and K_η.

3. APPLICATION TO Al–Li ALLOY

The case of the precipitation of metastable $L1_2$ ordered $\delta'(Al_3Li)$ particles from an f.c.c. disordered matrix in the Al–Li alloy system is particularly suited to this study. since isotropic interfacial energy is a very good approximation for this system and the elastic energy can be ignored. Furthermore. this system has been extensively studied recently [8]. which provides the necessary input information for the diffuse-interface model. For simplicity. we chose the mean field free energy in a second-neighbor interaction model as the local free energy density function [9].

$$f(c,\eta) = \frac{1}{2v_a}[(12W_1 + 6W_2)c^2$$
$$+ 3(-4W_1 + 6W_2)\eta^2]$$
$$+ \frac{k_B T}{4v_a}[(c + 3\eta)\ln(c + 3\eta)$$
$$+ (1 - (c + 3\eta))\ln(1 - (c + 3\eta))$$
$$+ 3(c - \eta)\ln 3(c - \eta)$$
$$+ 3(1 - (c - \eta))\ln(1 - (c - \eta))]\qquad(9)$$

where W_1, W_2 are first- and second-neighbor effective interchange energies. η is the long-range order parameter for the $L1_2$ phase. c is the average composition. k_B is the Boltzmann constant. v_a is the volume per atom and T is the temperature. Although it has been well understood that the above mean field free energy incorrectly gives a second-order order–disorder phase transition. when it is supposed to be first order. at composition $c = 0.5$. yet with the proper choice of W_1 and W_2. it can provide a reasonably good approximation of the low-temperature two-phase $(\alpha + \delta')$ field. which is of practical interest and of interest to the present study [9]. Moreover. a more accurate free energy density function is not expected to change the main conclusions of this paper—that is. while the exact values for the order parameter and composition of the critical nucleus might be different. the qualitative features of the profiles and their dependence on temperature and composition would remain the same.

The gradient energy coefficients K_η and K_c can also be expressed in terms of the effective interchange energies and the interatomic distances [10]

$$K_c = -\frac{1}{3}\sum_i \rho_i^2 W_i$$

$$K_\eta = -\frac{1}{3}\sum_i \rho_i^2 W_i e^{-i k_0 \cdot r_i}\qquad(10)$$
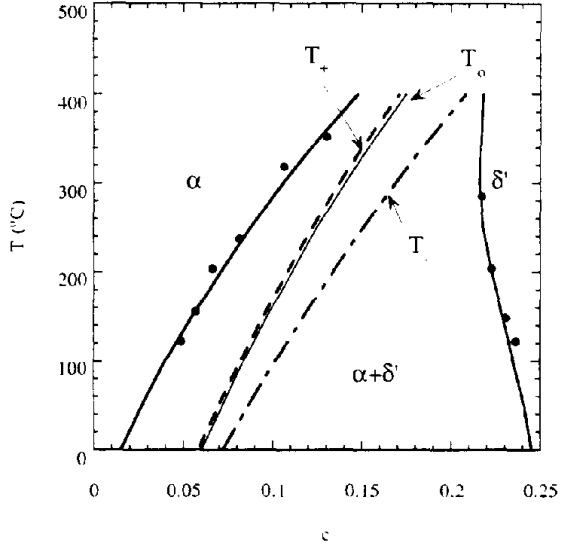

Fig. 2. The metastable two-phase field calculated from the free energy model (9). with interaction parameters from Ref. [11]: thick solid lines—the equilibrium phase boundaries: dashed line—disordering instability line of the ordered phase (T_+): thin solid line—the locus along which the free energies of the ordered and disordered phases are the same (T_0); and dot–dashed line—the ordering instability line (T_-). The approximate location of experimental points is also shown (after Ref. [9]).

where k_0 is the superlattice vector for the $L1_2$ ordered phase. ρ_1, ρ_2 etc. are the distances between nearest. second-nearest. etc. neighbors. and r_i is the corresponding lattice vector.

For convenience. we obtained the values of W_1 and W_2 from Ref. [11]. which gives $W_1 \sim 40.435\text{meV}/$ atom and $W_2 \sim -31.59\text{meV/atom}$. The gradient energy coefficients. K_η and K_c. calculated from this set of interchange energies. are equal to 14.422 and $-2.83\text{meV(nm)}^2/\text{atom}$. respectively. The low temperature part of the equilibrium phase diagram obtained using this free energy function is shown in Fig. 2. in which the dot dashed line (T_-) represents the ordering instability line below which a disordered phase is absolutely unstable with respect to ordering. the thin solid line (T_0) is the locus along which the ordered and disordered phases have the same free energy. the dashed line (T_+) is the disordering instability line above which an ordered phase is absolutely unstable with respect to disordering. and the solid lines are equilibrium phase boundaries.

With the local free energy density function. and the values of K_η and K_c. equations (8) were then solved using the subroutine COLSYS. developed by Ascher et al. [12]. which is designed to solve ordinary differential equations for systems of non-linear boundary-value problems. It uses the method of spline collocation at Gaussian points. in conjunction with a damped Newton's method. to solve non-linear problems. The subroutine subdivides the boundary interval into finer and finer grids until a user-specified
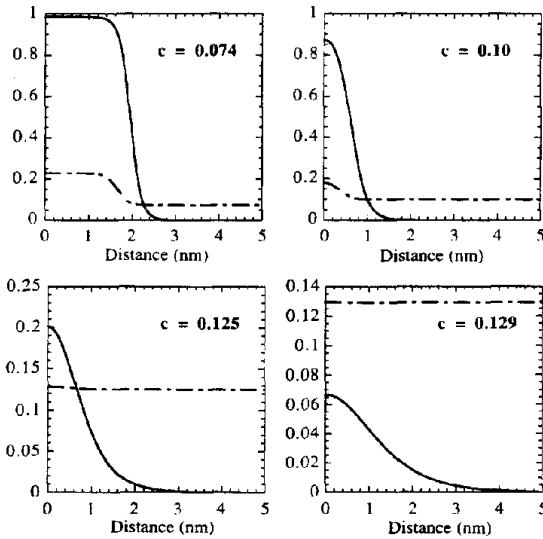
Fig. 3. Composition (dot–dashed) and order parameter (solid) profiles, at $T = 465K$.

Fig. 5. Composition (dot–dashed) and order parameter (solid) profiles, at $c = 0.12$.

tolerance is satisfied. To speed up the calculation, an initial guess of the profile was supplied. In our case, we assumed the initial profiles to be Gaussian with average at $r = 0$.

Figure 3 shows examples of critical composition and order parameter profiles for four different matrix compositions, obtained at a temperature of $T = 465K$. The free energy curves for the ordered and disordered phases as a function of composition at this temperature are shown in Fig. 4, at this temperature the equilibrium composition (Li in atomic or mole fraction) of the disordered phase (α), c_α, is ~ 0.068; the equilibrium composition of the metastable ordered phase δ', $c_{\delta'}$, is ~ 0.224; the composition at which the disordered phase becomes absolutely unstable with respect to δ' ordering, or the ordering instability composition, c_-, is ~ 0.131; the composition at which the δ' ordered phase is absolutely
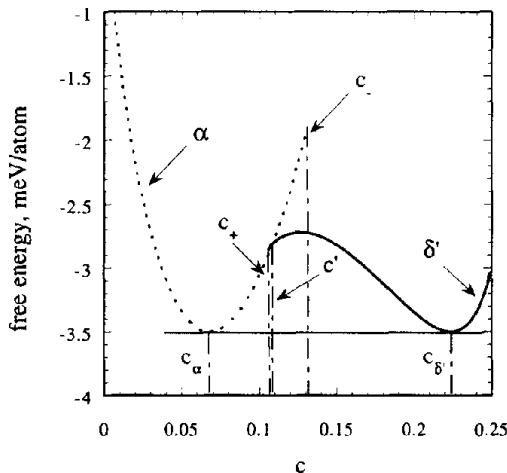

Fig. 4. Free energy–composition curves for the ordered and disordered phases at $T = 465K$.
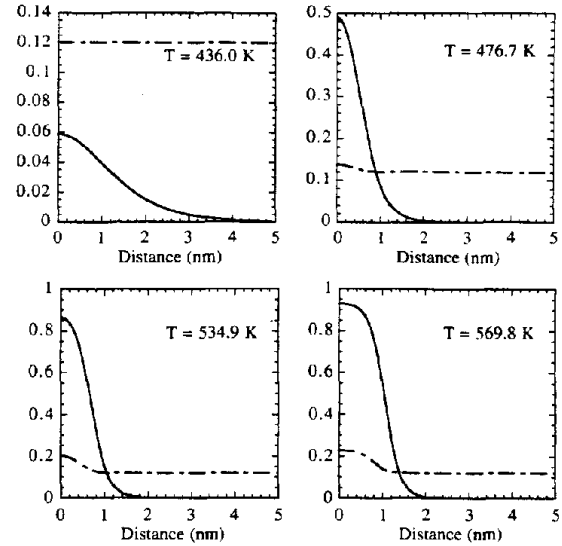
unstable with respect to disordering, c_+, is ~ 0.106; and the composition at which the ordered and disordered phases have the same free energy, c', is ~ 0.109. The order parameter profiles in Fig. 3 were actually η/c so as to make the values for the order parameter between 0.0 and 1.0 instead of between 0.0 and c. As the matrix composition increases, the composition and order parameter values at the center of a critical fluctuation decrease. Of the four cases shown in Fig. 3, only in the case which corresponds to matrix composition 0.074 are the order parameter and composition values at the center of the critical fluctuation close to the equilibrium values of the δ' ordered phase.

The equilibrium phase boundary of the disordered phase and the ordering instability line can also be approached by varying the temperature of the system, while keeping the matrix composition constant. The critical composition and order parameter profiles at four different temperatures at $c = 0.12$, are shown in Fig. 5. These critical profiles behave similarly to those in Fig. 3, i.e. the critical nucleus becomes increasingly non-classical, as the temperature is lowered from that close to the equilibrium phase boundary to that close to the ordering instability line.

The size of the critical fluctuations is arbitrarily defined as the radius at which the composition is equal to $(c_N + c_0)/2$ for the composition profile, and order parameter equal to $\eta_N/2$ for the order parameter profile, where c_N and η_N represent the values of the composition and order parameter at the center of the critical fluctuation, and c_0 is the matrix composition. The estimated sizes or radii of critical fluctuations as a function of matrix composition are plotted in Fig. 6. The size increases and diverges as the matrix composition approaches both the disordered phase boundary and the ordering instability
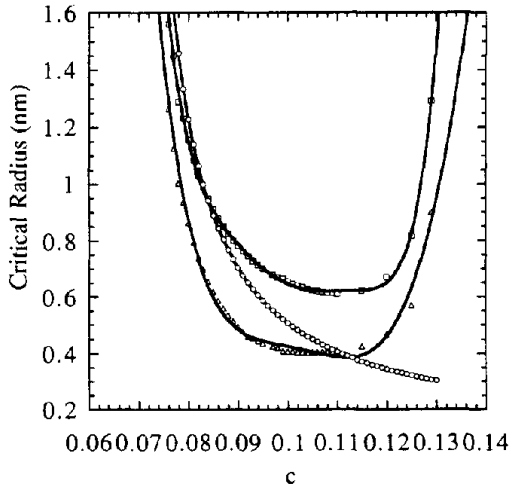
Fig. 6. The variation of the critical radius with composition: circles—classical; triangles—estimated from the critical composition profile; and squares—estimated from the critical order parameter profile.

Fig. 8. The variation of the nucleation rate with composition.

line. For comparison, the radius obtained using the classical nucleation theory is also plotted. For calculating the size of a classical nucleus, the interfacial energy is first calculated from a flat boundary between the equilibrium disordered phase and the δ' ordered phase. Then the driving force for nucleation is estimated by drawing a tangent line to the free energy curve of the disordered phase at the matrix composition, and calculating the largest difference between the free energy curve of the ordered phase and this tangent line. Finally, the free energy change for an ordered phase particle is calculated from the interfacial energy and the driving force, by assuming that the particle is spherical. The size of the critical nucleus can then be calculated by maximizing the free energy change with respect to the radius of the particle.

Figure 7 shows the critical free energy, calculated for different compositions, for the formation of both
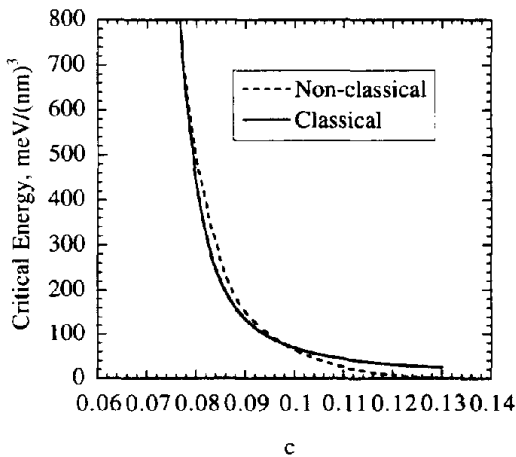

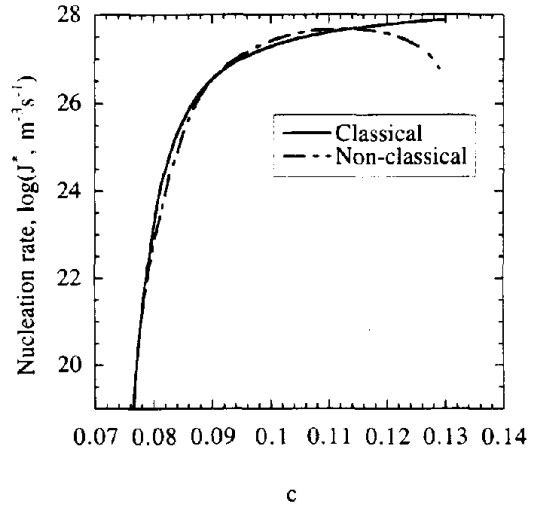Fig. 7. The variation of the critical energy of formation of a critical nucleus, with composition.

the non-classical and classical nuclei. The critical free energy for the former case can be calculated simply by substituting the gradients of the composition and order parameter profiles of Fig. 3 into equation (7), and summing over r. To calculate the latter curve, it is a simple matter of substituting the value of the critical radius into the free energy change expression. As expected, as the matrix composition increases, the critical free energy decreases. In the case of non-classical nucleation, the value for the critical free energy tends to zero as the ordering instability line is approached whereas in the classical case, the critical free energy remains finite.

With the values for the critical radii and the critical free energies of formation, it is possible to estimate the rate of nucleation, J^*, using the approach outlined by LeGoues et al. [13]. For both classical and non-classical nucleation, the nucleation rate is given as

$$J^* = Z\beta^* N_v \exp\left[\frac{-\Delta F^*}{k_B T}\right] \exp\left[\frac{-\tau}{t}\right] \quad (11)$$

where Z is the Zeldovich factor, ΔF^* is the critical free energy of formation of the nucleus, β^* is the impingement rate of atoms at the nucleus, N_v is the number of atoms per unit volume and k_B is the Boltzmann constant. The time dependency of the nucleation rate is incorporated into the second exponential, where τ is an incubation time, and t is the time for which nucleation has been taking place. Using a diffusion coefficient of $0.647 \text{nm}^2/\text{s}$ [14], Z, β^* and τ are calculated according to Ref. [13] as

$$Z = \frac{3v_a}{4\pi^{3/2}}\left[\frac{\Delta F^*}{k_B T}\right]^{1/2} \frac{1}{R^{*3}} \quad (12)$$

$$\beta^* = \frac{4\pi R^{*2} D c_0}{a^4} \quad (13)$$

$$\tau = \frac{32\pi a^4 R^{*4} k_B T}{3\Delta F^* v_a^2 D c_0} \qquad (14)$$

where D is the diffusion coefficient of solute atoms and a is the average of the lattice parameters of the nucleus and the matrix phases. The value of R^* used was that based upon the composition profiles. Figure 8 shows the nucleation rates obtained using this approach, for both the classical and the non-classical nucleation mechanisms. The time dependency of the nucleation rate has been ignored for both curves.

4. DISCUSSION

From the above calculations, it is demonstrated that a critical nucleus, or a critical fluctuation, consists of fluctuations in both the composition and order parameter profiles. Therefore, we cannot describe the non-classical nucleus of an ordered phase in a disordered matrix, using the composition profile alone. We have also demonstrated that the order parameter and the composition profiles become increasingly diffuse as the ordering instability or spinodal ordering line is approached, with their values at the center of the nucleus getting progressively closer to those of the matrix and the spatial extent of the nucleus approaching infinity. On the other hand, when the matrix composition is near the phase boundary of the disordered phase, the properties of the critical nucleus (composition and order parameter profiles) begin to resemble those of the equilibrium ordered (δ') phase, and we can define a "bulk" region of the critical nucleus and an "interface" between the nucleus and matrix, although the interface is diffuse. Therefore, it is expected that classical nucleation theory should apply in the composition region very close to the equilibrium phase boundary of the disordered phase. These
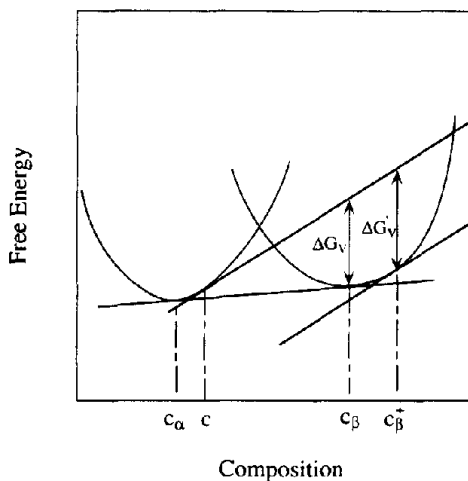

Fig. 9. The parallel tangent construction, showing that the driving force for nucleation is largest at a composition exceeding that of the equilibrium β phase.

results are similar to those obtained by Cahn and Hilliard for isostructural decomposition [1], with the matrix composition between the disordered phase boundary and the spinodal curve.

As mentioned above, when the matrix composition is very close to the phase boundary of the disordered phase, the composition and order parameter values at the center of the nucleus are essentially the same as those of the equilibrium ordered phase. However, a careful examination of the critical composition and order parameter profiles indicates that there is a range of matrix compositions for which the composition and the order parameter values within the critical nucleus may exceed those of the equilibrium ordered phase. This behavior seems to be consistent with the fact that the driving force for nucleation is a maximum when the composition within the nucleus is given by the parallel tangent construction (Fig. 9).

We showed that a critical nucleus contains both composition and order parameter fluctuations throughout the entire composition range that we studied, including the matrix compositions between c' and c_-. On the other hand, based on a thermodynamic stability analysis combining with some kinetic argument, Khachaturyan et al. [9] predicted that nucleation between c' and c_- would be congruent, i.e. a critical nucleus would only contain the order parameter fluctuation, while the composition was uniform in the nucleus, and the same as that of the matrix. We also compared the critical free energy values obtained for the two cases, i.e. for a critical nucleus with and without a composition fluctuation. To calculate the critical free energy for the latter case, we solved for the critical order parameter profile while keeping the composition uniform throughout the system. For matrix composition 0.12, we obtained a critical free energy of 14.482 meV/nm³ for the case with simultaneous composition fluctuation, which is lower than the 21.393 meV/nm³ obtained for the case of congruent nucleation. However, it should be emphasized that this analysis of the critical fluctuation is purely based on thermodynamics, whereas Khachaturyan's argument for congruent nucleation took into account the fact that ordering occurs faster than compositional clustering. Therefore, it is possible that more nuclei may develop from energetically less favorable but kinetically more favorable fluctuations than the critical ones. However, our computer simulations on the nucleation of δ' particles in Al–Li alloys using microscopic diffusion equations with random thermal noise terms, which take into account the kinetics, seem to confirm that there are coupled composition and order parameter fluctuations in the critical nucleus even in the matrix composition range between c' and c_-, although the composition fluctuation is very small in magnitude [15,16].

The critical radius, estimated from the critical fluctuations shown in Fig. 3, diverges as the matrix

composition approaches the ordering instability composition, c_- (see Fig. 6). This is consistent with the results of Cahn and Hilliard [1] and LeGoues et al. [2] for isostructural decomposition, when the matrix composition approaches the spinodal composition. However, as Binder [5] pointed out, this is an artifact arising from the fact that thermal fluctuations are ignored in the non-classical nucleation theory. He showed that the inclusion of a thermal noise term, as proposed by Cook [17], into the Cahn–Hilliard equation, did not produce this divergence. Similarly, the generalized nucleation theory, based on a cluster-dynamics approach, proposed by Binder et al. [18,19] did not predict the divergence at the spinodal composition. We have performed computer simulations of the nucleation process of δ' ordered phase from a disordered matrix, using the microscopic diffusion equations with random thermal noise. Indeed, our simulation results showed that the size of nuclei is finite at matrix compositions close to c_- [15,16].

5. CONCLUSIONS

The continuum non-classical nucleation theory of Cahn and Hilliard has been extended to the case of precipitation of ordered intermetallics from a disordered matrix in which a critical nucleus has to be described by both composition and order parameter profiles. Critical fluctuations of composition and order parameter profiles across a critical nucleus have been computed for matrix compositions varying from the disordered phase boundary to the ordering instability line. It is shown that only when the matrix composition is near the phase boundary of the disordered phase, the composition and order parameter values inside the nucleus are close to those of the equilibrium ordered phase, and the critical profiles become increasingly diffuse as the ordering instability line is approached. A critical nucleus consists of both composition and order parameter fluctuations through the entire composition range from the disordered phase boundary to the ordering instability line. Based on the non-classical nucleation theory, the size of critical fluctuations, the critical free energy change and the nucleation rate are also estimated for the particular

case of precipitation of δ' ordered from the disordered matrix in Al–Li alloy.

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