A theory of spinodal decomposition stabilized by coherent strain in binary alloys

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ABSTRACT

A phenomenological theory is developed which predicts the possible existence of meta-stable chemical composition modulations in the spinodal (instable) region of the phase diagram of binary alloys. This is accomplished through a modified elastic energy term in the theory of diffuse interfaces by Cahn and Hilliard: Analogously to Cahn's expansion of the molar chemical free energy, also the (un-relaxed) internal stress tensor due to chemical composition modulations is expanded in a Taylor series of the spatial derivatives of the local composition up to second order terms. This mathematical approach is confirmed by atomistic modeling.

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1. Introduction

For some binary alloys, experimental evidence was found that the short-range order state can be described not only by the atomic pair probability parameters (Warren parameters [1]) but also in terms of ordered micro-domains [2,3]. Aubauer [4,5] developed a phenomenological theory to explain this so-called state of "disperse order". He assumed a dilute system of equally sized domains with a trapezium shaped composition profile. Furthermore, he assumed that the ratio of the specific interface energy to the thickness of the rim zone be a constant. This ad hoc assumption is not evident, and indeed is not supported by Cahn's well-known theory of diffuse interfaces. Hence, Aubauer's theory was questioned [6], and the nature of short-range decomposition and short-range order was attributed solely to statistical composition fluctuations.

This discrepancy is resolved in the present paper by modifying the theory of Cahn and Hilliard [7–10]: In the same way as the local molar chemical energy, also the un-relaxed (distortion-free) internal stress tensor due to a given composition modulation is expanded in a Taylor series of the spatial derivatives of the local chemical composition up to second order terms. It is shown that this modified theory of diffuse interfaces can in principle explain the possible existence of meta-stable composition modulations in the spinodal region of the phase diagram of binary alloys, which are identified with short-range decomposition.

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2. Theory

2.1. Problem definition

A composition modulation $c(\mathbf{r})$ implies a (yet distortion-free) internal stress which together with an external pressure p_0 forms a stress field $\sigma^{(0)}$ (i.e. the 'un-relaxed state') which gives rise to a displacement field $\mathbf{u}(\mathbf{r})$ so that a point $\mathbf{r}$ is shifted to the point $\mathbf{r} + \mathbf{u}(\mathbf{r})$. The displacement field $\mathbf{u}(\mathbf{r})$ induces an elastic stress field $\sigma^{(\varepsilon)}$, and is determined by making the total stress $\sigma = (\sigma^{(0)} + \sigma^{(\varepsilon)})$ fulfill the elasto-mechanical equilibrium condition (stress relaxation). The thermodynamic equilibrium is characterized by a minimum of the mean molar Gibbs free energy. The mean molar Gibbs free energy G is composed of the mean molar chemical free energy F_{chem}, the mean molar elastic energy E_{elast}, and the product of the external pressure p_0 and the mean molar volume V:

$$G = F_{chem} + E_{elast} + p_0 \cdot V. \tag{1}$$

The local composition c is defined as the local mole fraction of the component B of the alloy AB, and is assumed to be a periodic function of the three spatial coordinates. Thus, the volume of the sample can be thought of being built up of equivalent unit domains with the same composition distribution. The material is taken to be isotropic, and the unit domains are approximated as spheres of equal size. In the un-relaxed state under pressure, the radius of these unit spheres is R. The total volume of all of the unit spheres is set equal to the volume of the sample. The boundary condition for each unit sphere is taken to be the same as for the whole

sample, i.e. the unit sphere is under the hydrostatic pressure p_0. In this way, the calculation of the mean molar Gibbs free energy G is approximately reduced to a spherical symmetric problem. The diameter of the unit sphere, $2R$, can be interpreted as the spatial period (or wave length) of the composition modulation which is described by the function $c(r)$ where r is the amount of the radius vector $\mathbf{r}$. The spherical composition distribution function $c(r)$ must fulfill the condition that the mean mole fraction of the component B in the unit sphere is equal to the constant alloy composition c_0:

$$\frac{3}{R^3} \cdot \int_0^R c(r) \cdot r^2 \cdot dr = c_0. \tag{2}$$

The equilibrium value of R, and the equilibrium function $c(r)$ are possibly obtained by minimizing G. This is a variational problem which is numerically solved by setting $c(r)$ to be a Fourier sum, thus making G approximately a function of a finite number of variables. For this purpose, the definition of $c(r)$, physically defined only in the range $0 \leqslant r \leqslant R$, is mathematically extended to $-R \leqslant r \leqslant R$ by the symmetry requirement $c(-r) = c(r)$, and to any value of r by the periodicity requirement $c(r + 2R) = c(r)$. Taking into account conditional Eq. (2), this Fourier sum can be written as

$$c(r) = c_0 - \frac{6}{\pi^2} \cdot \sum_{n=1}^{n_0} K_n \cdot \frac{\cos(n \cdot \pi)}{n^2} + \sum_{n=1}^{n_0} K_n \cdot \cos\left(\frac{n \cdot \pi \cdot r}{R}\right), \tag{3a}$$

where the $K_n (n = 1 - n_0)$ are Fourier coefficients, and n_0 is a sufficiently great number. In this way, G is approximated by a function of the independent variables R and the K_n.

Differentiation of $c(r)$ with respect to r yields:

$$\frac{dc}{dr} = -\frac{\pi}{R} \cdot \sum_{n=1}^{n_0} K_n \cdot n \cdot \sin\left(n \cdot \pi \cdot \frac{r}{R}\right), \tag{3b}$$

$$\frac{d^2c}{dr^2} = -\frac{\pi^2}{R^2} \cdot \sum_{n=1}^{n_0} K_n \cdot n^2 \cdot \cos\left(n \cdot \pi \cdot \frac{r}{R}\right), \tag{3c}$$

which is needed later.

2.2. The chemical free energy

According to Cahn and Hilliard [6], the local molar chemical free energy f is a function not only of the local composition c but also of the composition distribution in the immediate environment. Thus, f is a function of c as well as of the spatial derivatives of c. Straightforwardly, Cahn and Hilliard expanded f in a Taylor series of the spatial derivatives of c up to second order terms. For cubic crystal symmetry they obtained:

$$f = f_0(c) + \kappa_1 \cdot \nabla^2 c + \frac{1}{2} \cdot \kappa_2 \cdot (\nabla c)^2, \tag{4}$$

or, by applying the mathematical identity

$$\nabla(\kappa_1 \cdot \nabla c) = \kappa_1 \cdot \nabla^2 c + \frac{\partial \kappa_1}{\partial c} \cdot (\nabla c)^2, \tag{5}$$

$$f = f_0(c) + \nabla(\kappa_1 \cdot \nabla c) + \left(\frac{1}{2} \cdot \kappa_2 - \frac{\partial \kappa_1}{\partial c}\right) \cdot (\nabla c)^2, \tag{6}$$

where $f_0(c)$ is the molar chemical free energy of the homogeneous material of constant composition c under vacuum, and ∇ means the Nabla operator. The coefficients κ_1 and κ_2 are defined by:

$$\kappa_1 = \left(\frac{\partial f}{\partial\left(\frac{\partial^2 c}{\partial x_k^2}\right)}\right)_0, \tag{7a}$$

$$\kappa_2 = \left(\frac{\partial^2 f}{\partial\left(\frac{\partial c}{\partial x_k}\right)^2}\right)_0, \tag{7b}$$

which in general are dependent on c. The index "0" means that the differentiations are to be carried out in the homogeneous state of the material. The coordinates $x_k (k = 1,2,3)$ denote a right-handed Cartesian coordinate system with axes parallel to the crystallographic $\langle 1,0,0 \rangle$-directions.

The mean molar chemical free energy is given by

$$F_{\text{chem}} = \frac{1}{V_{\text{sample}}} \cdot \iiint_{\text{sample}} f \cdot dx_1 \, dx_2 \, dx_3, \tag{8}$$

where the integration is taken over the volume V_{sample} of the sample in the un-relaxed state. Substituting the expression on the right-hand side of Eq. (6) for f in Eq. (8) yields:

$$F_{\text{chem}} = \frac{1}{V_{\text{sample}}} \cdot \iiint_{\text{sample}} \left[f_0(c) + \left(\frac{1}{2} \cdot \kappa_2 - \frac{\partial \kappa_1}{\partial c}\right) \cdot (\nabla c)^2\right]$$
$$\cdot dx_1 \, dx_2 \, dx_3 + \frac{1}{V_{\text{sample}}} \cdot \iiint_{\text{sample}} \nabla(\kappa_1 \cdot \nabla c)$$
$$\cdot d\,x_1 \, d\,x_2 \, d\,x_3. \tag{9}$$

The second volume integral on the right-hand side of Eq. (9) can be transformed to an integral of $(\kappa_1 \cdot \nabla c)$ over the surface of the sample, and thus must be zero because there is no atomic diffusion through the surface of the sample ($\nabla c = 0$).

The final result for cubic crystal symmetry is then given by

$$F_{\text{chem}} = \frac{1}{V_{\text{sample}}} \cdot \iiint_{\text{sample}} \left[f_0(c) + \kappa \cdot (\nabla c)^2\right] \cdot dx_1 \, dx_2 \, dx_3, \tag{10}$$

where

$$\kappa = \frac{1}{2} \cdot \kappa_2 - \frac{\partial \kappa_1}{\partial c} \tag{11}$$

is still a function of c, but is set to be approximately constant for applications.

For a spherical symmetric composition distribution in an isotropic material, a local right-handed Cartesian coordinate system X_1, X_2, X_3 is used, with the X_3-axis in the radial direction, and the X_1- and X_2- axes tangent to the sphere r = const.. In this coordinate system, the spherical symmetry center is given by $O(0,0,-r)$. The mole fraction c at a position $P(x_1,x_2,x_3)$ is only dependent on its distance to the spherical symmetry center O, and thus is defined by the function

$$c = c\left[\sqrt{x_1^2 + x_2^2 + (x_3 + r)^2}\right]. \tag{12a}$$

The first and second partial derivatives of c with respect to x_1, x_2, x_3 at the position $(0,0,0)$ are obtained from Eq. (12a) by using the chain rule of differentiation:

$$\frac{\partial c}{\partial x_1} = 0, \quad \frac{\partial c}{\partial x_2} = 0, \quad \frac{\partial c}{\partial x_3} = \frac{dc}{dr}, \tag{12b}$$

$$\frac{\partial^2 c}{\partial x_1^2} = \frac{1}{r} \cdot \frac{dc}{dr}, \quad \frac{\partial^2 c}{\partial x_2^2} = \frac{1}{r} \cdot \frac{dc}{dr}, \quad \frac{\partial^2 c}{\partial x_3^2} = \frac{d^2c}{dr^2}, \tag{12c}$$

$$\frac{\partial^2 c}{\partial x_1 \partial x_2} = 0, \quad \frac{\partial^2 c}{\partial x_2 \partial x_3} = 0, \quad \frac{\partial^2 c}{\partial x_1 \partial x_3} = 0. \tag{12d}$$

Substituting the first partial derivatives from Eqs. (12b) for the gradient of c in Eq. (10), and replacing the volume element dxdydz by $4\pi r^2 dr$, and the volume of the sample by $4\pi R^3/3$, finally yields

$$F_{\text{chem}} = \frac{3}{R^3} \cdot \int_0^R \left[f_0(c) + \kappa \cdot \left(\frac{dc}{dr}\right)^2\right] \cdot r^2 \cdot dr, \tag{13}$$

since the unit sphere is supposed to represent the whole sample.

The function $f_0(c)$ is required to display the situation of spinodal decomposition exhibiting a miscibility gap: Two minima and one maximum in between define the A-rich phase and the B-rich phase