Computer Simulation of Phase Decomposition in Two Dimensions Based on a Discrete Type Non-linear Diffusion Equation[†]

Toshiyuki Koyama and Toru Miyazaki

*Department of Materials Science and Engineering, Nagoya Institute of Technology,
Nagoya 466, Japan*

In the present paper, we newly propose a comprehensive non-linear diffusion equation where atomic interaction parameters, elasticity, and mobility are assumed to depend on local composition to calculate the phase decomposition in actual alloy systems. The proposed non-linear diffusion equation is called "Discrete type non-linear diffusion equation" in the article. The phase decomposition in the Al-Zn and Fe-Mo binary systems are simulated in a two-dimensional medium by using their thermodynamic data consistent with the equilibrium phase diagrams. The microstructures theoretically obtained are well coincident with experimental results of these alloys. Especially, various morphological transformations such as the mottled and modulated structures by the spinodal decomposition, the particle shape change including splitting, directional alignment of precipitates, particle size uniformity, etc. are demonstrated.

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I. Introduction

The physical properties of a material depend not only on the crystal structure of constituent phases but also crucially on its microstructure. To design and obtain desirable materials properties, we have to understand and control the kinetics of structural transformations during practical heat treatment of alloys. However, phase transformations in real materials are often complicated with the appearance of various transient or metastable morphologies of microstructure. Especially, in solid-solid phase transformations, it is well known that the elastic strain due to the lattice mismatch between precipitates and matrix plays an important role in the morphological stability of microstructure⁽¹⁾⁻⁽⁵⁾. However, the quantitative understanding of the effects of elastic strains on thermodynamic phase equilibria as well as on detail dynamics of structural transformations is still insufficient.

The recent remarkable development of computers has enabled a numerical and detailed analysis of the dynamics of the structural transformation based on a nonlinear diffusion equation⁽⁶⁾⁻⁽¹³⁾. The computer simulation has become very useful in understanding the non-linear dynamics of phase decomposition in materials: not only in metallic alloys but also in ceramics⁽⁹⁾⁻⁽¹¹⁾ and polymer alloys⁽¹²⁾.

In the present paper, we propose a comprehensive non-linear diffusion equation where atomic interaction parameters, elasticity and mobility are assumed to depend on local composition to calculate the phase decomposition in actual alloy systems⁽⁶⁾⁻⁽⁹⁾. The proposed non-

linear diffusion equation is called "Discrete type non-linear diffusion equation" in the article. We demonstrate the two-dimensional computer simulations of phase decomposition in Al-Zn and Fe-Mo binary alloy systems on the basis of the proposed method. Various morphological transformations such as formation of mottled and modulated structures by the spinodal decomposition, the particle shape change including splitting, the directional alignment of precipitates, the particle size uniformity⁽¹⁾, etc. will be described.

II. Theoretical Basis

1. Definition of the discrete type non-linear diffusion equation

The non-linear kinetic equation employed in the present work is given by eq. (1).

$$\begin{aligned} \frac{\partial c(\mathbf{r}, t)}{\partial t} &= \text{div} [M\{c(\mathbf{r}, t), T\} \text{grad} \{\chi(\mathbf{r}, t)\}] \\ &= M\{c(\mathbf{r}, t), T\} \text{div} [\text{grad} \{\chi(\mathbf{r}, t)\}] \\ &\quad + \text{grad} [M\{c(\mathbf{r}, t), T\}] \cdot \text{grad} \{\chi(\mathbf{r}, t)\} \quad (1) \end{aligned}$$

where $c(\mathbf{r}, t)$ is the local composition at a position $\mathbf{r}$ and a time t . $M\{c(\mathbf{r}, t), T\}$ shows the mobility of atom diffusion. The diffusion potential $\chi(\mathbf{r}', t)$ is defined by eq. (2).

$$\begin{aligned} \chi(\mathbf{r}', t) &\equiv \left(\frac{\delta G_{\text{total}}}{\delta c} \right)_{\mathbf{r}=\mathbf{r}'} \\ &= \mu_c\{c(\mathbf{r}', t)\} + \mu_{\text{surf}}(\mathbf{r}', t) + \mu_{\text{str}}(\mathbf{r}', t) \quad (2) \end{aligned}$$

G_{total} is the total free energy consisting of the chemical free energy G_c , the interfacial energy E_{surf} and the elastic strain energy E_{str} as follows:

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$$G_{total} = G_c + E_{surf} + E_{str}. \quad (3)$$

Therefore, μ_c , μ_{surf} and μ_{str} in eq. (2) are given by the following equations, respectively:

$$\mu_c\{c(r', t)\} \equiv \left(\frac{\partial G_c}{\partial c} \right)_{r=r'} \quad (4)$$

$$\mu_{surf}(r', t) \equiv \left(\frac{\partial E_{surf}}{\partial c} \right)_{r=r'} \quad (5)$$

$$\mu_{str}(r', t) \equiv \left(\frac{\partial E_{str}}{\partial c} \right)_{r=r'}. \quad (6)$$

$M\{c(r, t), T\}$ in eq. (1) is concretely given by eq. (7) for an AB binary system⁽¹⁴⁾.

$$M\{c(r, t), T\} = [M_A(T)c(r, t) + M_B(T)\{1 - c(r, t)\}] \times c(r, t)\{1 - c(r, t)\}, \quad (7)$$

where $M_i(T)$ is the mobility of pure i -atom diffusion, which can be estimated from the self-diffusion coefficient $D_i(T)$.

The finite difference expression of eq. (1) leads

$$\begin{aligned} \frac{\partial c(r, t)}{\partial t} &= M\{c(r, t), T\} \text{div} [\text{grad} \{\chi(r, t)\}] \\ &+ \left\{ \frac{\partial M\{c(r, t), T\}}{\partial c} \right\} \text{grad} \{c(r, t)\} \cdot \text{grad} \{\chi(r, t)\} \\ &= M\{c(r, t), T\} \left[\sum_{r'} L_2(r-r') \chi(r', t) \right] \\ &+ \left\{ \frac{\partial M\{c(r, t), T\}}{\partial c} \right\} \left[\sum_{r'} L_1(r-r') c(r', t) \right] \\ &\cdot \left[\sum_{r'} L_1(r-r') \chi(r', t) \right], \end{aligned} \quad (8)$$

where $L_1(r-r')$ and $L_2(r-r')$ are the difference operators indicating the gradient and Laplacian, respectively, as described explicitly in the Section IV.

Equation (8) is a discrete type expression of the non-linear diffusion equation⁽⁶⁾⁻⁽⁸⁾. If the mobility is not a function of the local composition but that of an average composition, the second term of the right hand side in eq. (8) vanishes, and the eq. (8) becomes identical with the Khachaturyan diffusion equation⁽¹³⁾. It has already been demonstrated that the Khachaturyan diffusion equation is applicable to the calculation of the order-disorder phase transition process. Therefore, the order-disorder transformation can be also simulated by eq. (8), if the position vector r in eq. (8) is taken as the crystal lattice site, and the physical meaning of $c(r)$ changes from local composition to the single site occupation probability of finding a solute atom at the position r .

From the practical viewpoint of numerical analysis, eq. (8) is more useful than eq. (1) to describe the dynamics of many kinds of phase transformation processes, because the former is applicable not only to the atomic scale phase transformations such as order-disorder transitions but also to the mesoscopic scale phase transformations such as spinodal decomposition and precipitate

coarsening, etc. The term of “discrete” in “the discrete type non-linear diffusion equation” means the universality of the present calculation technique.

If the diffusion potential $\chi(r', t)$ at an arbitrary position r' in microstructure is obtained, $\partial c / \partial t$ can be evaluated from eq. (8), and consequently the temporal evolution of phase decomposition will be calculated by using the Euler technique.

$$c(r, t + \Delta t) = c(r, t) + \left\{ \frac{\partial c(r, t)}{\partial t} \right\}_t \Delta t \quad (9)$$

The precise evaluation of diffusion potential $\chi(r', t)$ is the most essential and important in the present simulation. The estimation of $\chi(r', t)$ for the diffusion controlled phase decomposition processes is represented in the next section.

III. Evaluation of the Diffusion Potential

1. Formulation of μ_c

In this study, the modified expression of the regular solution approximation is adopted as a chemical free energy, because we aim at the improvement of the simulation method for the phase decomposition, which is consistent with the equilibrium phase diagram of an actual alloy. The chemical free energy G_c is generally given by eq. (10)⁽¹⁵⁾. Henceforth, $c(r, t)$ is designated by $c(r)$.

$$\begin{aligned} G_c &= \frac{1}{2} \sum_r \Omega\{c(r), T\} c^2(r) \\ &+ \sum_r RT [c(r) \ln c(r) + \{1 - c(r)\} \ln \{1 - c(r)\}] \end{aligned} \quad (10)$$

The atomic interaction parameter $\Omega\{c(r), T\}$ is expanded into Taylor series with respect to $c(r)$.

$$\Omega\{c(r), T\} \equiv \sum_j \Omega_j(T) c^j(r) \quad (11)$$

where $\Omega_j(T)$ is the coefficient of the Taylor series, and j is an integer number. Substituting eqs. (10) and (11) to eq. (4), we get the chemical potential $\mu_c\{c(r')\}$ as follows:

$$\begin{aligned} \mu_c\{c(r')\} &= \sum_j \frac{j+2}{2} \Omega_j(T) c^{j+1}(r') \\ &+ RT [\ln c(r') - \ln \{1 - c(r')\}]. \end{aligned} \quad (12)$$

Since $\Omega_j(T)$ in eq. (11) can be obtained from the thermodynamic data of the equilibrium phase diagram easily, it is possible by using eq. (12) to get $\mu_c\{c(r')\}$ as a function of composition $c(r')$ at position r' .

2. Formulation of μ_{surf}

The interfacial energy E_{surf} is approximately defined by eq. (13)⁽¹⁶⁾.

$$\begin{aligned} E_{surf} &= \frac{1}{2} \sum_{p'} \sum_{p''} W(p' - p'', T) c(p') c(p'') \\ &- \frac{1}{2} \sum_{p'} \bar{W}(T) c^2(p'), \end{aligned} \quad (13)$$

where $\mathbf{p}'$ and $\mathbf{p}''$ are the position vectors of lattice site and $W(\mathbf{p}' - \mathbf{p}'', T)$ shows the atomic interaction energy. $c(\mathbf{p}')$ is the occupation probability of solute atoms on the lattice site at $\mathbf{p}'$. $\bar{W}(T)$ is the three-dimensional average of $W(\mathbf{p}' - \mathbf{p}'', T)$. Since $W(\mathbf{p}' - \mathbf{p}'', T)$ in eq. (13) and $\Omega_0(T)$ in eq. (11) is related to each other as described in eq. (14)⁽¹³⁾, $W(\mathbf{p}' - \mathbf{p}'', T)$ is evaluated by using the thermodynamic data $\Omega_0(T)$ on the equilibrium phase diagram. The detailed calculation procedure will be described in the next section.

$$\Omega_0(T) = \frac{1}{2} \sum_{\mathbf{p}' - \mathbf{p}''} W(\mathbf{p}' - \mathbf{p}'', T) \quad (14)$$

In eq. (13), the contribution of the $[\Omega_j(T), j \geq 1]$ to the interfacial energy is omitted. The higher order terms of $[\Omega_j(T), j \geq 1]$ originate in the multi-body interactions between three atoms or more. Since the interfacial energy is defined as the difference of the total internal energy from the bulk mean field value, we believe that the contribution of the interfacial energy to the total free energy change would be not so dominant especially for the phase decomposition in the disordered phases.

The Cahn-Hilliard's spinodal decomposition theory⁽¹⁴⁾, the TDGL model⁽¹⁷⁾ and the phase field method⁽¹⁸⁾⁽¹⁹⁾ define the interfacial energy as eq. (15) in contrast to eq. (13):

$$E_{surf} = \int_r \kappa \left(\frac{\partial c}{\partial r} \right)^2 dr, \quad (15)$$

where κ is the composition gradient energy coefficient, which is a function of $\Omega_0(T)$ and the inter-atomic distance⁽¹⁴⁾. Equation (15) is well known to be approximated by neglecting the higher order terms concerning the gradient and curvature of the concentration profile⁽¹⁴⁾. It is important to note that the omitted terms are included in eq. (13). Therefore, eq. (13) is considered to be more accurate than eq. (15).

The μ_{surf} is easily introduced by the eq. (16).

$$\mu_{surf}(\mathbf{p}') = \sum_{\mathbf{p}''} W(\mathbf{p}' - \mathbf{p}'', T) c(\mathbf{p}'') - \bar{W}(T) c(\mathbf{p}') \quad (16)$$

Furthermore, by using the Fourier transform of $W(\mathbf{p}' - \mathbf{p}'', T)$, the $\mu_{surf}(\mathbf{p}')$ at position $\mathbf{p}'$ is given by eq. (17). $V(\mathbf{h})$ and $Q_a(\mathbf{h})$ are defined by eqs. (18) and (19), respectively.

$$\mu_{surf}(\mathbf{p}') = \sum_{\mathbf{h}} [V(\mathbf{h}) - V(\mathbf{0})] Q_a(\mathbf{h}) \exp(i\mathbf{h}\beta\mathbf{p}') \quad (17)$$

$$V(\mathbf{h}) \equiv \sum_{\mathbf{p}' - \mathbf{p}''} W(\mathbf{p}' - \mathbf{p}'', T) \exp\{-i\mathbf{h}\beta(\mathbf{p}' - \mathbf{p}'')\} \quad (18)$$

$$Q_a(\mathbf{h}) \equiv \left(\frac{1}{N_a^3} \right) \sum_{\mathbf{p}''} c(\mathbf{p}'') \exp(-i\mathbf{h}\beta\mathbf{p}''), \quad (19)$$

where $\mathbf{h}$ is the wave number of a Fourier wave β which is defined by $\beta \equiv 2\pi/L$. L is the length of calculated volume in the real space, and N_a is the number of crystal lattice sites in L .

On the numerical calculation of the phase decomposition, we need a coarse grained expression $\mu_{surf}(\mathbf{r}')$ instead of the microscopic $\mu_{surf}(\mathbf{p}')$. In order to evaluate $\mu_{surf}(\mathbf{r}')$, the system is divided into several blocks larger than the unit cell of the crystal lattice, where $\mathbf{r}'$ is defined as a position vector to each block. Assuming that the solute concentration inside the individual block is uniform, eqs. (17) and (19) become eqs. (20) and (21), respectively. The details are explained in Appendix.

$$\mu_{surf}(\mathbf{r}') = \sum_{\mathbf{h}} [V(\mathbf{h}) - V(\mathbf{0})] Q(\mathbf{h}) \exp(i\mathbf{h}\beta\mathbf{r}') \quad (20)$$

$$Q(\mathbf{h}) \equiv \left(\frac{1}{N^3} \right) \sum_{\mathbf{r}''} c(\mathbf{r}'') \exp(-i\mathbf{h}\beta\mathbf{r}''), \quad (21)$$

where N is the number of blocks in L . A concrete evaluation of eq. (20) is explained in Section IV.

3. Formulation of μ_{str}

The elastic strain energy for the cubic lattice crystal is given by eq. (22) based on the Landau elasticity theory⁽²⁰⁾⁻⁽²²⁾, where C_{ijkl} is the elastic stiffness, e_{ij}^c is the constrained strain, and η is the lattice mismatch between A and B pure metals.

$$E_{str} = \sum_r \left[\begin{aligned} & \frac{3}{2} (C_{1111} + 2C_{1122}) \eta^2 \{c(\mathbf{r}) - c_0\}^2 - \eta (C_{1111} + 2C_{1122}) \{c(\mathbf{r}) - c_0\} \{e_{11}^c(\mathbf{r}) + e_{22}^c(\mathbf{r}) + e_{33}^c(\mathbf{r})\} \\ & + \frac{1}{2} C_{1111} \{e_{11}^{c^2}(\mathbf{r}) + e_{22}^{c^2}(\mathbf{r}) + e_{33}^{c^2}(\mathbf{r})\} + C_{1122} \{e_{11}^c(\mathbf{r})e_{22}^c(\mathbf{r}) + e_{22}^c(\mathbf{r})e_{33}^c(\mathbf{r}) + e_{33}^c(\mathbf{r})e_{11}^c(\mathbf{r})\} \\ & + 2C_{1212} \{e_{12}^{c^2}(\mathbf{r}) + e_{23}^{c^2}(\mathbf{r}) + e_{31}^{c^2}(\mathbf{r})\} \end{aligned} \right] \quad (22)$$

Here, the Vegard's law was assumed concerning the concentration dependence of the lattice constant. In addition, it is assumed that C_{ijkl} is proportional to the concentration as shown in eq. (23), where $C_{ijkl}^X(T)$ indicates the elastic stiffness constants of the pure X ($=A$ or B) metal, which are functions of temperature T .

$$C_{ijkl}\{c(\mathbf{r}), T\} = C_{ijkl}^A(T)\{1 - c(\mathbf{r})\} + C_{ijkl}^B(T)c(\mathbf{r}) = C_{ijkl}^0 + \Delta C_{ijkl}^{AB}\{c(\mathbf{r}) - c_0\} \quad (23)$$

$$C_{ijkl}^0 \equiv C_{ijkl}^A(T)(1 - c_0) + C_{ijkl}^B(T)c_0, \quad \Delta C_{ijkl}^{AB} \equiv C_{ijkl}^B(T) - C_{ijkl}^A(T) \quad (24)$$

When an ordered phase exists, these variables depend on not only the composition but also the degree of order. Then it is necessary to consider the degree of order dependence for these variables. However, only the concentration dependence was considered in the present work to make the calculation technique concise.

Substituting eq. (23) into eq. (22), we obtain the elastic strain energy as shown in eq. (25).

$$E_{str} = \sum_r \left[\begin{aligned} & (3/2)(C_{1111}^0 + 2C_{1122}^0)\eta^2 \{c(r) - c_0\}^2 - \eta(C_{1111}^0 + 2C_{1122}^0)\{c(r) - c_0\} \{e_{11}^c(r) + e_{22}^c(r) + e_{33}^c(r)\} \\ & + (1/2)C_{1111}^0 \{e_{11}^c(r) + e_{22}^c(r) + e_{33}^c(r)\} + C_{1122}^0 \{e_{11}^c(r)e_{22}^c(r) + e_{22}^c(r)e_{33}^c(r) + e_{33}^c(r)e_{11}^c(r)\} \\ & + 2C_{1212}^0 \{e_{12}^c(r) + e_{23}^c(r) + e_{31}^c(r)\} + (3/2)(\Delta C_{1111}^{AB} + 2\Delta C_{1122}^{AB})\eta^2 \{c(r) - c_0\}^3 \\ & - \eta(\Delta C_{1111}^{AB} + 2\Delta C_{1122}^{AB})\{c(r) - c_0\}^2 \{e_{11}^c(r) + e_{22}^c(r) + e_{33}^c(r)\} \\ & + (1/2)\Delta C_{1111}^{AB} \{c(r) - c_0\} \{e_{11}^c(r) + e_{22}^c(r) + e_{33}^c(r)\} \\ & + \Delta C_{1122}^{AB} \{c(r) - c_0\} \{e_{11}^c(r)e_{22}^c(r) + e_{22}^c(r)e_{33}^c(r) + e_{33}^c(r)e_{11}^c(r)\} \\ & + 2\Delta C_{1212}^{AB} \{c(r) - c_0\} \{e_{12}^c(r) + e_{23}^c(r) + e_{31}^c(r)\} \end{aligned} \right] \quad (25)$$

Substituting eq. (25) to eq. (6), we consequently obtain the $\mu_{str}(r')$ as eq. (26). The Landau elastic strain energy is expanded with composition c and e_{ij}^c , so that the $\mu_{str}(r')$ is easily expressed as indicated in eq. (26).

$$\begin{aligned} \mu_{str}(r') = & 3(C_{1111}^0 + 2C_{1122}^0)\eta^2 \{c(r') - c_0\} - \eta(C_{1111}^0 + 2C_{1122}^0)\{e_{11}^c(r') + e_{22}^c(r') + e_{33}^c(r')\} \\ & + \frac{9}{2}(\Delta C_{1111}^{AB} + 2\Delta C_{1122}^{AB})\eta^2 \{c(r') - c_0\}^2 - 2\eta(\Delta C_{1111}^{AB} + 2\Delta C_{1122}^{AB})\{c(r') - c_0\} \{e_{11}^c(r') + e_{22}^c(r') + e_{33}^c(r')\} \\ & + \frac{1}{2}\Delta C_{1111}^{AB} \{e_{11}^c(r') + e_{22}^c(r') + e_{33}^c(r')\} + \Delta C_{1122}^{AB} \{e_{11}^c(r')e_{22}^c(r') + e_{22}^c(r')e_{33}^c(r') + e_{33}^c(r')e_{11}^c(r')\} \\ & + 2\Delta C_{1212}^{AB} \{e_{12}^c(r') + e_{23}^c(r') + e_{31}^c(r')\} \end{aligned} \quad (26)$$

The constrained strain $e_{kl}^c(r')$ in eq. (26) is given by eq. (27) on the basis of the microelasticity theory⁽²³⁾.

$$e_{kl}^c(r') = \sum_h \frac{1}{2} C_{pqmn}^0 \eta_{mn} \{n_q G_{pl}(\mathbf{n}) n_k + n_q G_{pk}(\mathbf{n}) n_l\} \times Q(\mathbf{h}) \exp(i\mathbf{h}\beta\mathbf{r}') \quad (27)$$

$$G_{il}^{-1}(\mathbf{n}) \equiv C_{ijk}^0 n_j n_k \quad (28)$$

$\mathbf{n}$ is the unit vector of $\mathbf{h}$. The function $G_{il}(\mathbf{n})$ in eq. (27) is the inverse matrix of $G_{il}^{-1}(\mathbf{n})$ which is defined by eq. (28). Calculating eq. (27), we obtain the constrained strain $e_{kl}^c(r')$ at an arbitrary position in the microstructure, and substituting elements of them into eq. (26), we obtain $\mu_{str}(r')$ at the position r' .

Thus, $\mu_c(r')$, $\mu_{surf}(r')$, and $\mu_{str}(r')$ are obtained. Here it should be noted that these potentials are given as functions of position r' , so that the diffusion potential $\chi(r')$ can be evaluated at each position in the microstructure.

IV. Calculation Method in Two Dimensions

The evaluation method of $\chi(r')$ for the two-dimensional (2-D) phase decomposition is explained in detail. The chemical potential, $\mu_c(r')$ can be evaluated at an arbitrary position r' by employing eq. (12) when $\Omega_j(T)$ is obtained from the thermodynamic data of the equilibrium phase diagram. In order to calculate the numerical value of the $\mu_{surf}(r')$, $Q(\mathbf{h})$ and $V(\mathbf{h})$ should be formulated. The former can numerically be evaluated by the Fast

Fourier Transformation of the composition field $c(r')$. The latter is analytically obtained as described below. Here, $W(i \geq 3)$ is assumed to be zero⁽²⁴⁾ and the value of $\Omega_0(T)$ is assigned only to the first and second nearest neighbor atomic interaction energies $W(1)$ and $W(2)$. The ratio of $W(1)/W(2)$ should be $\sqrt{2}$ if the interfacial energy density is isotropic in a 2-D square lattice⁽¹⁶⁾.

$$W(1) = \frac{\Omega_0(T)}{(2 + \sqrt{2})}, \quad W(2) = \frac{W(1)}{\sqrt{2}} \quad (29)$$

The assumption of the isotropy of the interface energy density is approved approximately for the phase separation process⁽¹⁾. Using the above two assumptions, we can determine $W(1)$ and $W(2)$ from the value of $\Omega_0(T)$. Thus $V(\mathbf{h})$ is given by eq. (30):

$$V(\mathbf{h}) = 2W(1)\{\cos(h_x\beta d_1) + \cos(h_y\beta d_1)\} + 4W(2)\cos(h_x\beta d_1)\cos(h_y\beta d_1), \quad (30)$$

where h_x and h_y are the components of the wave vector $\mathbf{h}$ [$\mathbf{h} = (h_x, h_y)$]. The term d_1 in eq. (30) is the inter-atomic distance of the first nearest neighbors in the 2-D square lattice used in the present calculation. Consequently, we get $\mu_{surf}(r')$ at position r' numerically, by the inverse Fourier transformation of the product of $V(\mathbf{h})$ and $Q(\mathbf{h})$.

Finally, $\mu_{str}(r')$ is dealt with. In the 2-D system, the relaxation of strain component along the z -axis ($=e_{33}^c = e_{3i}^c$) should be zero. Therefore, eq. (26) is rewritten to eq. (31) for 2-D.

$$\begin{aligned} \mu_{str}(r') = & 3(C_{1111}^0 + 2C_{1122}^0)\eta^2 \{c(r') - c_0\} - \eta(C_{1111}^0 + 2C_{1122}^0)\{e_{11}^c(r') + e_{22}^c(r')\} \\ & + \frac{9}{2}(\Delta C_{1111}^{AB} + 2\Delta C_{1122}^{AB})\eta^2 \{c(r') - c_0\}^2 - 2\eta(\Delta C_{1111}^{AB} + 2\Delta C_{1122}^{AB})\{c(r') - c_0\} \{e_{11}^c(r') + e_{22}^c(r')\} \\ & + \frac{1}{2}\Delta C_{1111}^{AB} \{e_{11}^c(r') + e_{22}^c(r')\} + \Delta C_{1122}^{AB} e_{11}^c(r')e_{22}^c(r') + 2\Delta C_{1212}^{AB} e_{12}^c(r') \end{aligned} \quad (31)$$

The explicit forms of constrained strain of eq. (27) are given by eq. (32) for the case of pure dilatation of eigen strain.

$$e_{11}^c(\mathbf{r}') = \eta(C_{1111}^0 + 2C_{1122}^0) \sum_h Z_{11}(\mathbf{n}) Q(\mathbf{h}) \exp(i\mathbf{h}\beta\mathbf{r}') \quad (32a)$$

$$e_{22}^c(\mathbf{r}') = \eta(C_{1111}^0 + 2C_{1122}^0) \sum_h Z_{22}(\mathbf{n}) Q(\mathbf{h}) \exp(i\mathbf{h}\beta\mathbf{r}') \quad (32b)$$

$$e_{12}^c(\mathbf{r}') = e_{21}^c(\mathbf{r}') = \eta(C_{1111}^0 + 2C_{1122}^0) \sum_h Z_{12}(\mathbf{n}) Q(\mathbf{h}) \exp(i\mathbf{h}\beta\mathbf{r}') \quad (32c)$$

$$Z_{11}(\mathbf{n}) = \frac{[1 + \xi n_1^2] n_1^2}{[C_{1111}^0 + \xi(C_{1111}^0 + C_{1122}^0) n_1^2 n_2^2]} \quad (33a)$$

$$Z_{22}(\mathbf{n}) = \frac{[1 + \xi n_2^2] n_2^2}{[C_{1111}^0 + \xi(C_{1111}^0 + C_{1122}^0) n_1^2 n_2^2]} \quad (33b)$$

$$Z_{12}(\mathbf{n}) = \frac{(2 + \xi) n_1 n_2}{2[C_{1111}^0 + \xi(C_{1111}^0 + C_{1122}^0) n_1^2 n_2^2]} \quad (33c)$$

$$\xi \equiv \frac{C_{1111}^0 - C_{1122}^0 - 2C_{1212}^0}{C_{1212}^0} \quad (34)$$

Thus, the constrained strain at position $\mathbf{r}'$, $e_{ij}^c(\mathbf{r}')$, is numerically evaluated by the inverse fast Fourier transformation of $Z_{ij}(\mathbf{n}) Q(\mathbf{h})$ estimated from eqs. (32) and (33), then the $\mu_{str}(\mathbf{r}')$ at position $\mathbf{r}'$, $\mu_{str}(\mathbf{r}')$ is given by substituting $e_{ij}^c(\mathbf{r}')$ into eq. (31). Consequently, the diffusion potential $\chi(\mathbf{r}')$ is obtained as the sum of the three potentials $\mu_c(\mathbf{r}')$, $\mu_{surf}(\mathbf{r}')$, and $\mu_{str}(\mathbf{r}')$. Since the composition $c(\mathbf{r}')$ at the arbitrary position $\mathbf{r}'$ is given, the phase decomposition process is evaluated by numerical calculation on the basis of the difference method. The difference calculation in eq. (8) for 2-D simulation is given by the next equations:

$$L_2(\mathbf{r}-\mathbf{r}')\varphi(\mathbf{r}') = \frac{1}{b_1^2} [\varphi(x+b_1, y) + \varphi(x-b_1, y) + \varphi(x, y+b_1) + \varphi(x, y-b_1) - 4\varphi(x, y)] \quad (35a)$$

$$L_1(\mathbf{r}-\mathbf{r}')\varphi(\mathbf{r}') = \left(\frac{\varphi(x+b_1, y) - \varphi(x-b_1, y)}{2b_1}, \frac{\varphi(x, y+b_1) - \varphi(x, y-b_1)}{2b_1} \right), \quad (35b)$$

where b_1 is defined by L/N . $\varphi(\mathbf{r}')$ is either $\chi(\mathbf{r}')$ or $c(\mathbf{r}')$, x and y are the components of the vector $\mathbf{r}$.

Since the present calculation will be performed in the 2-D, the precise value of the time is not so important. So we assume $M_A(T) = M_B(T) = M_0(T)$ in eq. (7) for simplicity, and the time t is normalized by b_1^2/D_0 , where D_0 is the self diffusion coefficient defined by $D_0 = M_0(T)RT$. The unit of the normalized time is designated by (s') in this paper. The dynamics of the phase decomposition when the values of $M_A(T)$ and $M_B(T)$ are remarkably different is a very interesting problem, the simulation results will be reported in another article in the future.

The computer used in the present work is a workstation [Indy(175 MHz R4400SC), SGI]. The calculation time required to the 2-D simulation for the individual alloy is about 12 h. The processing performance of the computer is still insufficient for the 3-D simulation. The progress of the computer is so remarkable that we expect the 3-D calculation will become practical in the very near future.

V. Calculation Results for the Al-Zn and Fe-Mo Binary Alloy Systems

1. Al-21.2 at% Zn alloy

According to a lot of previous investigations on the microstructure of the Al-Zn alloy system, it is well known that isotropic Guinier-Preston zones are formed by the phase decomposition, resulting in a mottled microstructure⁽¹⁴⁾.

Figure 1 shows the phase diagram of Al-Zn alloy system⁽²⁵⁾, where the dotted line and the chain line are chemical binodal and spinodal lines, respectively. The calculation

was performed for an alloy indicated by a solid circle in the diagram, i.e., $c_0 = 0.212$ at 373 K. The chemical free energy function which explains the chemical binodal line of α phase (fcc) is given by eq. (36)⁽²⁶⁾:

$$G_c = a_0(T)c^2 + a_1(T)c^3 + RT[c \ln(c) + (1-c) \ln(1-c)]$$

$$a_0(T) = -25571 + 17.951T \quad (\text{J/mol})$$

$$a_1(T) = 15771.6 - 20.526T \quad (\text{J/mol}). \quad (36)$$

The atomic interchange energies $W(1)$ and $W(2)$ are evaluated by using $a_0(T)$ values in eq. (36) on the basis of eq. (29). Other numerical values⁽²⁷⁾ used in the calculation are listed in Table 1. The elastic stiffness constants of pure Al are substituted for those of Al-21.2 at% Zn alloy.

Fig. 1 Equilibrium phase diagram of the Al-Zn system. A solid circle shows the chemical composition for the computer simulation. The broken and chained lines are metastable chemical binodal and spinodal lines of the α (Al) phase, respectively.

Table 1 Numerical values used for the calculation.

Alloy System	Al-Zn	Fe-Mo
Temperature, T/K	373	773
Alloy composition, c_0	0.212	0.2–0.5
Elastic stiffness, (X=Al, Fe, Mo)		
$C_{11}^X/10^4 \text{ MN} \cdot \text{m}^{-2}$	10.7(Al)	23.3(Fe), 46.3(Mo)
$C_{12}^X/10^4 \text{ MN} \cdot \text{m}^{-2}$	6.07(Al)	13.5(Fe), 16.1(Mo)
$C_{44}^X/10^4 \text{ MN} \cdot \text{m}^{-2}$	2.82(Al)	11.8(Fe), 10.9(Mo)
Lattice mismatch, η	0.0257	0.083
Interatomic distance, $d_1/10^{-9} \text{ m}$	0.405	0.286
Calculation area, $L/10^{-9} \text{ m}$	120	120
Number of Fourier wave, $N \times N$	256×256	256×256
Distance for difference, $b_1/10^{-9} \text{ m}$	0.469	0.469

loy. The elastic anisotropy factor, $A=1.22$, suggests that the alloy is almost isotropic in the elasticity. The initial composition fluctuations before aging were generated according to random numbers of the computer, whose total amplitude from the average alloy concentration is approximately 1%.

The temporal evolution of phase decomposition calculated for the Al-Zn alloy is represented in Fig. 2, where the dark region corresponds to the solute-rich zone, completely white means pure Al, and completely black is pure Zn. The squares inside the each figure show the power spectrum of the microstructure. It is clearly recognized from Fig. 2(a) through (f) that the solute-rich zones are gradually formed (b), the percolated mottled structures appear (c), and then these solute-rich regions become isolated (d), (e) and (f). The microstructures are morphologi-

cally isotropic and gradually coarsen with the competitive growth⁽²⁸⁾ among zones, as is clearly recognized from the power spectra inserted in each picture.

The calculated microstructures are very similar to the experimentally obtained microstructure under the same condition with the calculation⁽¹³⁾. The predominant wavelength of spinodal decomposition is 4 nm in the calculation, which approximately coincides with the experiments.

2. Fe-Mo alloys

Figure 3 shows the phase diagram of the Fe-Mo binary alloy system⁽²⁹⁾, where the dotted line and the chain line are the metastable coherent binodal and spinodal lines, respectively. The lines are unsymmetrical about $c=0.5$, because of proportional increment of elastic constants with Mo content. The chemical free energy of α phase is given by eq. (37)⁽²⁹⁾:

$$G_c = a_0 c^2 + RT [c \ln(c) + (1-c) \ln(1-c)]$$

$$a_0 = -36490.7 \quad (\text{J/mol}). \quad (37)$$

The numerical values⁽²⁷⁾ used in the calculation for the Fe-Mo system are summarized in Table 1. It should be noted that the lattice mismatch η is fairly large in the Fe-Mo system⁽²⁹⁾. The computer simulations of phase decomposition were performed at the solid marks inside the spinodal line. The initial composition fluctuations before aging were generated in the same way as in the preceding calculation for Al-Zn.

The time evolution of microstructure calculated for the Fe-20 at%Mo alloy is presented in Fig. 4, where the black parts indicate the Mo-rich region. The phase decomposition is clearly recognized to progress with ag-

Fig. 2 Time evolution of the phase decomposition calculated for the Al-21.2 at%Zn aged at 373 K.

Fig. 3 Equilibrium phase diagram of the Fe-Mo system. The broken and chained lines are metastable coherent binodal and spinodal lines of the α (A2) phase, respectively.

ing time. Since the Fe-Mo alloy system has a large lattice mismatch, the Mo-rich zones along $\langle 10 \rangle$ directions, *i.e.* the $\langle 10 \rangle$ modulated structure, is produced during phase decomposition. The morphological changes are clearly reflected to the power spectra shown in the figures. The maximum peak intensity appears along the $\langle 10 \rangle$ direction at the initial stage of spinodal decomposition. In the coarsening stage, the competitive growth between particles takes place as indicated by arrows in Fig. 4(e). Some rows of precipitates are vanished, and the maximum peaks in the power spectrum move toward the center.

A TEM microphotograph of Fe-20 at%Mo alloy aged under the same condition with the computation has shown a $\langle 100 \rangle$ modulated structure whose wavelength is

about 4.0 nm⁽²⁹⁾. The interparticle spacing of calculated microstructure, about 5.5 nm, which coincides approximately with that of the experimental value.

Figure 5 shows the calculated microstructures of Fe-30 at%Mo alloy, where the periodic modulations along the $\langle 10 \rangle$ direction are also observed. With progress of aging the precipitates are competitively coarsened by the mechanism of dislocation climbing⁽¹⁶⁾, so that the precipitates become more cuboid in shape and more periodic in alignment. The precipitates are almost uniform in shape and in size as is obviously recognized in Figs. 5(e) and (f). Such specific behavior of precipitate coarsening is due to the elastic interaction energy between the precipitates. It has been known that the uniformity in particle size is explained well by the shape bifurcation theory of the particle coarsening proposed by us⁽¹⁾.

Figure 6 represents the micrographs of Fe-40 at%Mo alloy, which is approximately in the center of miscibility gap. Since the volume fraction of precipitates becomes higher, the encounter of precipitates happens so that the rod-shaped particles are temporarily produced in many places, as seen in Fig. 6(d). However, in further aging the particle-splitting can be observed as indicated by arrows in Fig. 6(f). It suggests that uniformity of particle size caused by the elastic interactions becomes energetically dominant than the usual particle coarsening controlled by the interfacial energy⁽¹⁾⁽³⁾. The figures from (d) to (f) clearly show that the microstructure is self-regulated by the elastic interaction energy so as to produce a periodic microstructure with uniform particle size.

Figure 7 shows the microstructural development of Fe-50 at%Mo alloys with aging time. In this case, the Mo-rich phase exceeds 50% in volume fraction (see Fig. 3). Therefore, white Fe-rich precipitates are formed as the

Fe-20at %Mo, $T=773K$

Fig. 4 Time evolution of the phase decomposition calculated for the Fe-20 at%Mo aged at 773 K.

Fe-30at %Mo , T=773K

Fig. 5 Time evolution of the phase decomposition calculated for the Fe-30 at%Mo aged at 773 K.

Fe-40at %Mo , T=773K

Fig. 6 Time evolution of the phase decomposition calculated for the Fe-40 at%Mo aged at 773 K.

precipitate phase at the early stage of phase decomposition (see Figs. 7(b) and (c)), but become connected with each other so as to form thin films wrapping the Mo-rich zones; the elastically hard Mo-rich phase is covered with the elastically soft Fe-rich phase.

The reason why such a structure is formed is that the composition dependence of the elastic constant is introduced in the present calculation⁽⁷⁾. The constrained strain is concentrated on the elastically soft Fe-rich phase as already discussed by Onuki⁽²²⁾. As the result, the con-

strained strain in a hard Mo-rich phase is relatively released. Therefore, the total elastic strain energy of the microstructure decreases, then the characteristic morphology of microstructure is stabilized. A quantitative analysis concerning this interesting phenomenon is now under investigation, the results of which will be reported elsewhere in the future. The identical microstructures have experimentally been recognized in many real alloy systems such as Ni-base⁽¹⁾ and Fe-base⁽²⁴⁾ alloys.

Fig. 7 Time evolution of the phase decomposition calculated for the Fe-50 at%Mo aged at 773 K.

VI. Conclusion

A discrete type non-linear diffusion equation is newly proposed. The composition dependence of the atomic interchange energy, mobility and the elasticity are also taken into account so as to be applicable for the phase decomposition in real alloy systems. The phase decomposition processes in the Al-Zn and Fe-Mo binary systems are demonstrated in the 2-D simulations with their thermodynamic data related to the equilibrium phase diagrams. The microstructures numerically simulated are well coincident with the experimental results of these alloys. Especially, the features of the microstructural evolution in elastically constrained system agree remarkably well with the experimental observations that have already been obtained.

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Appendix

The derivation of eq. (20) is explained in this appendix. At first, in order to define the coarse-grained composition field, the microstructure is divided into several blocks, which are called "super cells". The size of the super cells is larger than the unit cell of the crystal lattice,

and $\mathbf{r}'$ is defined as the position vector to each super cell. The vector to the crystal lattice site $\mathbf{p}'$ is defined by eq. (A1):

$$\mathbf{p}' = \mathbf{r}' + \mathbf{q}'. \quad (\text{A1})$$

Then, the vector $\mathbf{q}'$ in eq. (A1) is the position vector from point $\mathbf{r}'$ to the crystal lattice site $\mathbf{p}'$. Substituting eq. (A1) into eq. (17) in the text, and using eq. (19), we obtain eq. (A2).

$$\begin{aligned} \mu_{surf}(\mathbf{p}') &= \sum_{\mathbf{h}} [V(\mathbf{h}) - V(\mathbf{0})] Q_a(\mathbf{h}) \exp(i\mathbf{h}\beta\mathbf{p}') \\ &= \sum_{\mathbf{h}} [V(\mathbf{h}) - V(\mathbf{0})] \left[\left(\frac{1}{N_a^3} \right) \sum_{\mathbf{p}'} c(\mathbf{p}') \exp(-i\mathbf{h}\beta\mathbf{p}') \right] \exp(i\mathbf{h}\beta\mathbf{p}') \\ &= \sum_{\mathbf{h}} [V(\mathbf{h}) - V(\mathbf{0})] \left[\left(\frac{1}{N_a^3} \right) \sum_{\mathbf{r}'' + \mathbf{q}''} c(\mathbf{r}'' + \mathbf{q}'') \exp\{-i\mathbf{h}\beta(\mathbf{r}'' + \mathbf{q}'')\} \right] \exp\{i\mathbf{h}\beta(\mathbf{r}' + \mathbf{q}')\} \\ &= \sum_{\mathbf{h}} [V(\mathbf{h}) - V(\mathbf{0})] \left[\left(\frac{1}{N_a^3} \right) \sum_{\mathbf{r}'' + \mathbf{q}''} c(\mathbf{r}'' + \mathbf{q}'') \exp\{-i\mathbf{h}\beta(\mathbf{q}'' - \mathbf{q}')\} \exp(-i\mathbf{h}\beta\mathbf{r}'') \right] \exp(i\mathbf{h}\beta\mathbf{r}') \\ &= \sum_{\mathbf{h}} [V(\mathbf{h}) - V(\mathbf{0})] \left\{ \left(\frac{1}{N^3} \right) \sum_{\mathbf{r}''} \left[\left(\frac{1}{N_q^3} \right) \sum_{\mathbf{q}''} c(\mathbf{r}'' + \mathbf{q}'') \exp\{-i\mathbf{h}\beta(\mathbf{q}'' - \mathbf{q}')\} \right] \exp(-i\mathbf{h}\beta\mathbf{r}'') \right\} \exp(i\mathbf{h}\beta\mathbf{r}'), \quad (\text{A2}) \end{aligned}$$

where N_a and N are the number of unit cell and the super cell in the length of L , respectively. N_q is defined by $N_q \equiv N_a/N$. The average composition $\bar{c}(\mathbf{r}'')$ in each super cell denoted by $\mathbf{r}''$ is given by eq. (A3):

$$\bar{c}(\mathbf{r}'') = \left(\frac{1}{N_q^3} \right) \sum_{\mathbf{q}''} c(\mathbf{r}'' + \mathbf{q}''). \quad (\text{A3})$$

Here, we assume that the composition inside the super cell is uniform, so $c(\mathbf{r}'' + \mathbf{q}'')$ in the eq. (A2) is replaced by the $\bar{c}(\mathbf{r}'')$. Hence, by using eq. (A3) and the orthogonality between the Fourier waves, the following equation will be derived:

$$\begin{aligned} \left(\frac{1}{N_q^3} \right) \sum_{\mathbf{q}''} c(\mathbf{r}'' + \mathbf{q}'') \exp\{-i\mathbf{h}\beta(\mathbf{q}'' - \mathbf{q}')\} &\equiv \left(\frac{1}{N_q^3} \right) \sum_{\mathbf{q}''} \bar{c}(\mathbf{r}'') \exp\{-i\mathbf{h}\beta(\mathbf{q}'' - \mathbf{q}')\} \\ &= \left(\frac{1}{N_q^3} \right) \sum_{\mathbf{q}'} \left[\left(\frac{1}{N_q^3} \right) \sum_{\mathbf{q}''} c(\mathbf{r}'' + \mathbf{q}'') \right] \{-i\mathbf{h}\beta(\mathbf{q}'' - \mathbf{q}')\} = \left(\frac{1}{N_q^3} \right) \sum_{\mathbf{q}'} \left[\left(\frac{1}{N_q^3} \right) \sum_{\mathbf{q}''} c(\mathbf{r}'' + \mathbf{q}'') \exp(-i\mathbf{h}\beta\mathbf{q}'') \right] \exp(i\mathbf{h}\beta\mathbf{q}') \\ &= \left(\frac{1}{N_q^3} \right) \sum_{\mathbf{q}'} c(\mathbf{r}'' + \mathbf{q}') = \bar{c}(\mathbf{r}''). \quad (\text{A4}) \end{aligned}$$

Since $\bar{c}(\mathbf{r}'')$ is the coarse-grained local composition in the microstructure, we can rewrite $\bar{c}(\mathbf{r}'')$ as $c(\mathbf{r}'')$. The Fourier transform of the $c(\mathbf{r}'')$ is defined by eq. (21) in the text, substituting eqs. (A4) and (21) into eq. (A2) leads eq. (A5):

$$\begin{aligned} \mu_{surf}(\mathbf{p}') &= \mu_{surf}(\mathbf{r}' + \mathbf{q}') \\ &= \sum_{\mathbf{h}} [V(\mathbf{h}) - V(\mathbf{0})] Q(\mathbf{h}) \exp(i\mathbf{h}\beta\mathbf{r}'). \quad (\text{A5}) \end{aligned}$$

It should be noted that the variable $\mathbf{q}'$ is vanished on the

right-hand side of eq. (A5), so $\mu_{surf}(\mathbf{r}' + \mathbf{q}')$ takes a same value on each crystal lattice site $\mathbf{p}' (= \mathbf{r}' + \mathbf{q}')$ inside the super cell denoted by $\mathbf{r}'$. As a consequence, eq. (20) is derived.

The coarse-grained operation, eq. (A3), ignores the composition fluctuation inside the super cell, hence, it is very important to understand that the interfacial energy originated in the composition fluctuation inside the super cell assumed to be 0 by the coarse-grained approximation.