TOPICAL REVIEW

Phase-field modeling of microstructure evolutions in magnetic materials

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Abstract
Recently, the phase-field method has been extended and utilized across many fields of materials science. Since this method can incorporate, systematically, the effect of the coherency induced by lattice mismatch and the applied stress as well as the external electrical and magnetic fields, it has been applied to many material processes including solidification, solid-state phase transformations and various types of complex microstructure changes. In this paper, we focus on the recent phase-field simulations of real magnetic materials, and the simulation method for magnetic materials is explained comprehensively. Several applications of the phase-field method to clarifying the microstructure changes in magnetic materials, such as Ni$_2$MnGa ferromagnetic shape memory alloy, FePt nanogranular thin film, Co–Sm–Cu rare-earth magnet, Fe–Cr–Co spinodal magnet, and Fe–C steel with external magnetic field, are demonstrated. Furthermore, the general concept of the effective strategy for controlling microstructure in magnetic materials is proposed.

Keywords: phase transformation, phase decomposition, pattern formation, micromagnetics, simulation, diffusion equation, evolution equation, free energy

1. Introduction

In the last two decades, the phase-field approach [1, 2] has become a useful and powerful tool for understanding and modeling phase transformations and microstructure evolutions across many fields in materials science, and several review articles [3–6] and textbooks [7–12] regarding the phase-field method are now available. The meaning of phase field is the spatial and temporal order-parameter field defined in a continuum diffused interface model. By using the phase-field order parameters, various types of complex microstructure changes observed in materials science can be efficiently described.

Up to the present, the phase-field models have been successfully applied to a wide range of material microstructure formations. Dendrite growth during the solidification of pure metal and alloys is the main target of this method, where the phase-field simulation is widely accepted for calculating mesoscopic pattern formations. After the great success in solidification, researchers in the field of solid–solid phase transformations started using the name ‘phase-field method’ for their dynamic simulations of phase transformations and microstructure changes, because the basic calculation theory of the phase-field method is almost the same as their popular kinetic approach, i.e. the simulation of phase transformations using the Cahn–Hilliard diffusion equation [13] and Allen–Cahn relaxation equation [14]. As a consequence, the application area of the phase-field method is now extended greatly as follows: solidification process [15–19], spinodal decomposition [20–23], coarsening of precipitate phase [24–27], tweed and twin microstructure formation [28–30] by martensitic transformations which include a shape memory effect and polarization domain pattern dynamics observed in ferroelectric structural phase transition, grain growth and...
recrystallization [31–34], dislocation dynamics [35–36], crack propagation behavior [37], and morphological microstructure changes under external magnetic, electric and stress fields [38–41], for example. Furthermore, the phase-field crystal method [42] that can directly treat the atomic probability density at the crystal lattice site has recently been proposed as a new extension of the traditional phase-field formalism. Note that the subjects above, in effect, cover all contents in a textbook of materials science and engineering, so that the phase-field approach has been gaining an important position in the comprehensive computational investigation in materials science. In the history of the developmental process of phase-field methodology, the most important breakthrough must be the asymptotic analysis connecting the phase-field equations with sharp interface models in the computationally tractable ‘thin interface’ limits [43–45]. This theoretical basis has been helpful in making the phase-field method a practical tool for quantitative modeling of phase transformations and microstructure evolutions.

The fundamental calculation theory and the simulation techniques surrounding the phase-field method have mostly been established up to now. Since phase-field methodology enables us to model complex microstructure changes quantitatively, it will be possible to search for the most desirable microstructure using this method as a design simulation, i.e. through computer trial-and-error testing. Therefore, the most effective strategy for developing advanced materials is as follows: firstly, we elucidate the mechanism of microstructure changes experimentally, then we model the microstructure evolutions quantitatively using the phase-field method based on the experimental results, and finally, we search for the most desirable microstructure while simultaneously considering both the simulation and experimental data. However, there are few phase-field simulations applied directly to quantitative microstructure design in real materials. In this paper, as typical examples of quantitative phase-field modeling applied to complex microstructure changes in real alloy systems, the recent simulation results of the phase transformations and microstructure evolutions in magnetic materials are demonstrated, and the effective strategy for controlling microstructure in magnetic materials is proposed.

2. Phase-field method

2.1. Definition of order parameters in magnetic materials

In the conventional phase-field approach, the definition of the order parameter is the first important step. The order parameters describing the microstructure changes in multicomponent and multiphase systems with paramagnetic states are the composition field $c_i(r, t)$ and the phase field $s_i(r, t)$, where $r = (x, y, z)$ is a local position vector and is time. The subscript $i$ of $c_i(r, t)$ is an integer number indicating the number of components in the system, i.e. $i = 1, 2, \ldots, N_c$ for an $N_c$-component system, whereas the subscript $i$ of $s_i(r, t)$ is an integer number distinguishing each phase in the microstructure, i.e. $i = 1, 2, \ldots, N_r$ for an $N_r$-phase system. The physical meaning of $s_i(r, t)$ is the probability of finding phase $i$ at position $r$ and time $t$, so its range is defined as $0 \leq s_i(r, t) \leq 1$. In order to describe the ferromagnetic phase, another order parameter, $M(r, t)$, that is, the magnetic moment vector [46], is introduced to deal with local spontaneous magnetization in the microstructure. The magnetic moment vector $M(r, t)$ is often defined as $M(r, t) = \int M(r, t) m(r, t)$, where $m(r, t)$ is a unit vector along vector $M$, and the quantity $M(r, t)$ means the degree of local magnetization, $M(r, t) = |M(r, t)|$. Note that $M(r, t)$ is described as a function of $c_i(r, t)$ and $s_i(r, t)$, i.e. $M(r, t) = M[c_i(r, t), s_i(r, t)]$. For instance, when a ferromagnetic phase is precipitated from the supersaturated solid solution of paramagnetic matrix during diffusion phase decomposition, $M(r, t)$ is a function of local composition $c_i(r, t)$. In the case of the martensitic transformation from the paramagnetic parent phase to the ferromagnetic product phase, $M(r, t)$ becomes a function of $s_i(r, t)$ which is a phase-field order parameter corresponding to the probability of finding the martensitic phase. Therefore, the independent variables to describe phase transformations and microstructure changes relevant to ferromagnetic phases are $c_i(r, t)$, $s_i(r, t)$ and $m(r, t)$, and the total free energy of the phase transformed heterogeneous microstructure is described by using these parameters. The spatial and temporal evolutions of these order parameters correspond to the dynamics of phase transformation and are simulated on the basis of the governing differential equations explained in the next section.

2.2. Governing equations

The conventional phase-field method is a continuum model to simulate morphological microstructure evolutions using field variables. The differential equations describing spatial and temporal dynamics of the field variables are derived assuming the maximum energy dissipation of the system [4]. In general, the field variables are classified into two types, i.e. the conserved and nonconserved variables. The conserved fields $c_i$ evolve with time according to the following Caahn–Hilliard equation (equation (1)) [13], and the non-conserved fields $s_i$ are governed by the Allen–Cahn equation (equation (2)) [14].

$$\frac{\partial c_i(r, t)}{\partial t} = \nabla \left\{ M_{ij} \left[ \nabla \frac{\delta G_{\text{sys}}}{\delta c_j(r, t)} + \xi_c(r, t) \right] \right\}, \tag{1}$$

$$\frac{\partial s_i(r, t)}{\partial t} = -L_{ij} \left[ \frac{\delta G_{\text{sys}}}{\delta s_j(r, t)} + \xi_s(r, t) \right]. \tag{2}$$

In this paper, the conserved field $c_i$ is a local composition and the nonconserved field $s_i$ corresponds to a phase field. The microstructure evolution of a system can be calculated by numerically solving the above equations with respect to appropriate initial and boundary conditions. The symbols $M_{ij}$ and $L_{ij}$ are the mobility of atom diffusion and the relaxation coefficient, respectively. $G_{\text{sys}}$ is the total free energy of an inhomogeneous microstructure, and $\xi_p$ is the Gaussian thermal noise for order parameter $p$ (either $c_i$ or $s_i$). The normalized magnetic moment vector $m(r, t)$ is one of the main variables for the simulation of magnetic materials. The temporal and spatial dynamics of $m(r, t)$ are...
calculated on the basis of the Landau–Lifshitz equation or Landau–Lifshitz–Gilbert equation [47, 48].

In order to calculate microstructure changes quantitatively, the precise evaluation of total free energy \(G_{ SYS}\) is the most important step. The formulation of the total free energy of magnetic materials, particularly with a focus on the magnetic energy, is explained in the next section.

### 2.3. Formulation of total free energy of magnetic materials

The total free energy of the microstructure, \(G_{ SYS}\), is given as

\[
G_{SYS} = G_c + E_{grad} + E_{str} + E_{mag},
\]

where \(G_c\) is the mean field chemical free energy, and \(E_{grad}\) is the gradient energy [13] induced from the spatial inhomogeneity of order parameter fields in the microstructure. The elastic strain energy \(E_{ str}\) is evaluated by using the micro-elasticity theory [49] which is sometimes called ‘Micromechanics’ [50], where the eigenstrain [50] is defined as a function of the order parameters. \(E_{ str}\) also includes mechanical potential energy when the external stress is applied. \(E_{mag}\) is a magnetic energy depending on the magnetic domain morphology in the microstructure and the external magnetic field, which is evaluated on the basis of the micromagnetic theory [47, 48], which is sometimes called ‘Micromagnetics’ [46–48]. The following are the details of \(G_c\) and \(E_{mag}\) in equation (3), which are directly related to magnetic energy. The details of the formulation of \(E_{grad}\) and \(E_{str}\) are available in [11].

The mean field chemical free energy of the multicomponent and multiphase systems is expressed as

\[
G_c = \int r \left[ \sum_{j=1}^{N_i} h[s_j(r,t)]G_c^0[c_j(r,t)] + W[s_i(r,t)] \right] \text{dr},
\]

where \(G_c^0[c_j(r,t)]\) is the Gibbs energy of the \(\alpha_j\) phase. The practical form of \(G_c^0[c_j(r,t)]\) is available as a function of composition and temperature from the thermodynamic database of the equilibrium phase diagram developed by the CLPHAD (calculation of phase diagrams) approach [51]. \(h[s_j(r,t)]\) is defined as a monotonic function [3–12] with respect to \(s_j\), which satisfies the conditions \(h(s_j = 0) = 0\) and \(h(s_j = 1) = 1\). \(W[s_i(r,t)]\) is a penalty term [3–12] prohibiting the coexistence of different phases at the same position in a microstructure at one time, and satisfies \(W(s_i = 0) = 0\) and \(W(s_i = 1) = 0\). When we consider the ferromagnetic single phase \(\alpha\) in an \(A-B\) binary alloy as a simple example, the Gibbs energy \(G_c^0[c_j(r,t), T]\) is given by the subregular solution approximation [51] as

\[
G_c^0(c, T) = \frac{G_{A}^0(T)}{1 - c} + G_{B}^0(T) + L(c, T)c(1 - c) + RT \ln c + (1 - c) \ln(1 - c)] + G_{mag}^0,
\]

where \(c\) is the composition of component B, \(R\) is the gas constant, and \(T\) is the absolute temperature. The functions \(G_{A}^0(T)\) and \(G_{B}^0(T)\) are Gibbs energies of pure A and B metals, respectively, and depend on temperature. The interaction parameter \(L(c, T)\) is a function of composition and temperature. The last term of the right-hand side, \(G_{mag}^0\), is the magnetic contribution to Gibbs energy, and it is defined as

\[
G_{mag}^0 = RT \ln [\beta(c) + f\{\tau(c, T)\}].
\]

The quantity \(G_{mag}^0\) means, physically, the amount of Gibbs energy change during the phase transition from the paramagnetic to the ferromagnetic state. \(\beta(c)\) is the atomic magnetization normalized to the Bohr magneton, and \(\tau\) is a dimensionless temperature defined as \(\tau(c, T) = T/T_c(c)\), where \(T_c(c)\) is the Curie temperature. Both \(\beta(c)\) and \(T_c(c)\) are obtained as functions of composition. The explicit form of the function \(f(\tau(c, T))\) is given in [52] as a function of \(\tau\).

The materials parameters in \(G_{A}^0\), \(G_{B}^0\), \(L(c, T)\), \(\beta(c)\) and \(T_c(c)\) are obtained from the thermodynamic database of equilibrium phase diagrams [51].

Since \(G_{mag}^0\) is the Gibbs energy of the ferromagnetic \(\alpha\) phase which has a single magnetic domain and an infinite specimen size, \(G_{mag}^0\) is taken as a standard energy reference for evaluating magnetic energy \(E_{mag}\) in equation (3). As a consequence, \(E_{mag}\) is defined as an excess magnetic energy depending on the morphologies of the magnetic domain microstructure and the external applied magnetic field. According to Micromagnetics [46–48], \(E_{mag}\) is written as

\[
E_{mag} = E_{ext} + E_{exch} + E_{an} + E_{mstr} + E_d,
\]

where \(E_{ext}\) is the Zeeman energy from an external magnetic field, \(E_{exch}\) the excess exchange energy in the magnetic domain wall region, (a mean field exchange energy is included in \(G_{mag}^0\)), \(E_{an}\) the magnetocrystalline anisotropy energy, \(E_{mstr}\) the magnetostriction energy, and \(E_d\) the magnetostatic energy. The explicit form of these terms is given as

\[
E_{ext} = -\frac{1}{\mu_0} \int \mathbf{M}(r,t) \cdot \mathbf{H}_{ext} \text{dr},
\]

\[
E_{exch} = \int r \left[ A[M(r,t)] \left[ |\nabla m_1(r,t)|^2 + |\nabla m_2(r,t)|^2 \right] + |\nabla m_3(r,t)|^2 \right] \text{dr},
\]

\[
E_{an} = \int r K_u[M(r,t)] \left[ 1 - \mathbf{m}(r,t) \cdot \mathbf{e}_{an} \right] \text{dr},
\]

\[
E_{mstr} = \frac{1}{2} \int r \left[ C_{ijkl} \left( \varepsilon_{ij}^{muc}(r,t) - \varepsilon_{ij}^{muc}(r,t) \right) \right] \times \left[ \varepsilon_{kl}^{muc}(r,t) - \varepsilon_{kl}^{muc}(r,t) \right] \text{dr},
\]

\[
E_{d} = -\frac{1}{2} \int r K_d[M(r,t)] \mathbf{m}(r,t) \cdot \mathbf{h}_d(r,t) \text{dr}.
\]

The above expression of \(E_{an}\) is assumed to be for the case of simple uniaxial anisotropy, and \(\mu_0\) is the permeability of vacuum. The exchange stiffness coefficient \(A\), magnetocrystalline anisotropy coefficient \(K_u\), and magnetostatic energy coefficient \(K_d\) are, respectively, expressed as

\[
A[M(r,t)] = \frac{a_{exch} M^2(r,t)}{\mu_0}, \quad K_u[M(r,t)] = \frac{M^2(r,t)}{\mu_0},
\]

\[
K_d[M(r,t)] = \frac{M^2(r,t)}{\mu_0}.
\]
where $a_{\text{exch}}$ and $k_a$ are the dimensionless material constants. The stray field $h_{\text{sd}}(\mathbf{r}, t)$ is evaluated on the basis of the dipole-dipole interaction among magnetic moments in the microstructure and calculated using \[ h_{\text{sd}}(\mathbf{r}, t) = -\int \frac{d\mathbf{r}'}{4\pi} \left( \frac{\mathbf{m}(\mathbf{r}', t) \cdot \mathbf{r}' - 3(\mathbf{r} - \mathbf{r}') \cdot \mathbf{m}(\mathbf{r}', t) - \mathbf{r}' - \mathbf{r}}{|\mathbf{r} - \mathbf{r}'|^3} \right) \cdot \mathbf{r}' \right) \] (10)

$H_{\text{ext}}$ is the applied external magnetic field, and $\mathbf{e}_{\text{m}}(\mathbf{r}, t)$ is the unit vector along the easy axis of magnetization at position $\mathbf{r}$ and time $t$, and depends on the local crystal orientation. If the phase field $s_i(\mathbf{r}, t)$ indicates a local crystal orientation [31–34], $\mathbf{e}_{\text{m}}(\mathbf{r}, t)$ is given as a function of $s_i(\mathbf{r}, t)$. In equation (8), magnetostriction energy $E_{\text{mstr}}$ is expressed by the formalism used in Micromechanics [49, 50], where $C_{ijkl}$, $\varepsilon'^{\text{m}}_{ij}(\mathbf{r})$ and $\varepsilon^{\text{m0}}_{ij}(\mathbf{r})$ are the elastic stiffness, the constrained strain, and the eigenstrain induced by magnetostriction, respectively, and $\varepsilon^{\text{m0}}_{ij}(\mathbf{r})$ is assumed to be a function of $M(\mathbf{r}, t)$ [53].

It should be emphasized that each magnetic energy in equation (8) is proportional to $M^2(\mathbf{r}, t)$. In the phase-field methodology, it is easy to treat the condition $M(\mathbf{r}, t)$, which depends on the order parameters $c_i(\mathbf{r}, t)$ and $s_i(\mathbf{r}, t)$, so that the microstructure developments affected by magnetic energy are calculated reasonably well.

3. Evaluation of saturation magnetization and effective microstructure control using magnetic effects

3.1. Evaluation of saturation magnetization dependent on order parameters

Saturation magnetization is a function of order parameters such as temperature and composition. An important point is that the saturation magnetization as a function of composition is available from the thermodynamic database of phase diagrams [51]. Since the function $\beta(c)$ in equation (6) is the atomic magnetization normalized to the Bohr magneton, the saturation magnetization $M$ dependent on temperature and composition is given as

$$M(c, T) = \beta_B \beta(c) I(\tau(c, T)),$$

where $\beta_B$ is the value of the Bohr magneton and $\tau(c, T)$ is given by $\tau(c, T) = T/T_c(c)$. The Curie temperature $T_c(c)$ and the function $\beta(c)$ are obtained from the thermodynamic database of phase diagrams as functions of composition. The function $I(\tau)$ is a dimensionless spontaneous magnetization that is usually expressed using the Langevin function or Brillouin function [46], and an approximate expression of $I(\tau)$ tractable for computing has also been proposed [54]. Equation (11) is extremely worthwhile and useful, because we can calculate the magnetization value at any temperature and composition in real magnetic alloys.

3.2. Effective strategy for controlling microstructure using magnetic effects

Since the local magnetization $M(\mathbf{r}, t)$ depends, in general, on the order parameters $c_i(\mathbf{r}, t)$ and $s_i(\mathbf{r}, t)$, the phase transformations and the microstructure changes, i.e. temporal and spatial developments of $c_i(\mathbf{r}, t)$ and $s_i(\mathbf{r}, t)$, are influenced by the magnetic energy. However, the amount of each form of magnetic energy in equation (8) is often very small compared with the conventional chemical driving force for phase transformations. Therefore, the appropriate boundary conditions should be selected in order to control microstructure changes using such weak magnetic energy. The promising boundary conditions applicable for magnetic materials design are summarized below.

3.2.1 Choosing the temperature and alloy composition near the phase transition point. In order to change the phase transformation behavior drastically using a small amount of magnetic energy, it is useful to choose the temperature and alloy composition near the phase transition point on the phase diagram. Since the Gibbs energy change required for phase transition is small in the vicinity of the phase transition point on the phase diagram, the phase transition behavior is affected significantly even if the magnetic energy is weak. This concept is valid for controlling the martensite variant exchange behavior observed in ferromagnetic shape memory alloy under external magnetic field [55].

3.2.2 Make use of critical point of nucleation. It is often observed that several equivalent variants appear during martensitic transformation. A typical example is found in the cubic → tetragonal martensitic transformation, where three equivalent variants of the tetragonal product phase having their $c$-axes along $x$-, $y$-, and $z$-directions arise with equal probability during martensitic transformation. This symmetry of the formation of equivalent variants will easily be broken if a small fluctuation is applied just at the critical stage of tetragonal phase nucleation [56]. If the external magnetic field is applied along the $x$-direction to the cubic paramagnetic phase in which the nucleation of the ferromagnetic tetragonal phase is imminent, the tetragonal phase with the $c$-axis along the $x$-direction will appear preferentially, where the easy axis of magnetization is the $c$-axis. This variant selection at the nucleation stage takes place even if the magnetic energy is very weak.

3.2.3 Using the phase transformation near the magnetic transition point (near the Curie point). It can be seen from equations (8) and (9) that the magnetic energy is proportional to $M^2(\mathbf{r}, t)$. If we assume $M(\mathbf{r}, t)$ to be a linear function with respect to solute composition $c(\mathbf{r}, t)$, Taylor expansion gives

$$M(c(\mathbf{r}, t)) = M_0(c_0) + \frac{\partial M}{\partial c} c_0(c(\mathbf{r}, t) - c_0),$$

$$M^2(c(\mathbf{r}, t)) = M_0^2(c_0) + 2\frac{\partial M}{\partial c} c_0 M_0(c_0)(c(\mathbf{r}, t) - c_0) + \left(\frac{\partial M}{\partial c}\right)^2 c_0^2(c(\mathbf{r}, t) - c_0)^2.$$
where \( c_0 \) is the average composition; then, the volume integral of \( M^2(r, t) \) provides
\[
\int r M^2(c(r, t)) \, dr = M_0^2(c_0) + \left( \frac{\partial M}{\partial c} \right) c_0 \int r (c(r, t) - c_0)^2 \, dr.
\]
(12)

Note that the quantity \( \partial M/\partial c \) in the second term of the right-hand side becomes an extremely large value when the alloy composition \( c_0 \) is coincidence with the Curie point on the phase diagram [57]. It is well known that the quantity \( \partial M/\partial T \) diverges at the Curie temperature [46], and this divergence behavior also takes place for \( \partial M/\partial c \) at the alloy composition corresponding to the Curie point on the phase diagram. It is important to realize that the quantity \( \partial M/\partial c \) becomes large enough to affect the microstructure changes even when the amount of magnetic energy itself is quite small. A typical example is the magnetic aging used in the microstructure control of spinodal magnets such as ALNICO alloys [58]. As can be seen in equation (12), the second term of the right-hand side is proportional to \((\partial M/\partial c)^2\), therefore, both the appearance and the annihilation of a magnetic moment, i.e. \( \partial M/\partial c > 0 \) and \( \partial M/\partial c < 0 \), exert some effect on the phase transformations. Furthermore, although the magnetic energy is vanishingly small in a paramagnetic state just beyond the Curie point, \((\partial M/\partial c)^2\) remains large near the Curie temperature, which enables us to control the microstructure, even in the paramagnetic state, using magnetic energy.

4. Simulation of phase transformations and microstructure changes in real magnetic materials

In this section, as a typical example of the quantitative phase-field modeling applied to complex microstructure changes in real materials, the recent simulation results of the phase transformations and microstructure evolutions in magnetic materials are demonstrated.

4.1. Microstructure changes in Ni_{52}Mn_{48} ferromagnetic alloy under external stress and magnetic fields

Since Ullakko et al found the magnetic shape memory effect in Ni_{52}Mn_{48} alloy [59], considerable attention has been focused on clarifying the nature of the magnetic-field-induced gigantic strain and on searching for similar ferromagnetic shape memory materials, because the response of the magnetic shape memory effect is much faster than that of the normal thermal shape memory effect. For this reason, the Ni_{52}Mn_{48} alloy system has been actively investigated [60]. Because the microstructure changes are affected by various factors, e.g. external magnetic field, applied stress, internal stress, driving force for martensitic transformation, and mobility of twin boundary motion, the quantitative modeling of the complex microstructure changes is useful and necessary for understanding the nature of the magnetically induced shape memory effect. In what follows, we show the simulation results of quantitative phase-field modeling of macrostructure changes in Ni_{52}Mn_{48}; the details of the calculation model can be found in [55].

Figure 1 shows the development of the twin domain microstructure in the tetragonal Ni_{52}Mn_{48} phase under external applied stress and magnetic fields calculated on the basis of the two-dimensional phase-field simulation [55]. The white and black parts in the figure correspond to the twin domains with tetragonal orientations of the \( c \)-axis along the horizontal and vertical directions, respectively. The microstructure changes in figures 1(a)–(c) show the twin domain growth under the condition of 1MPa compressive stress \( \sigma^A \) applied along the vertical direction. Note that the black domain preferentially grows accompanying the twin boundary movement, because the tetragonality of the Ni_{52}Mn_{48} phase is less than unity and the \( c \)-axis of the black domain is along the vertical direction, i.e. the compressive force makes black domains more energetically stable than the white domains. On the other hand, figures 1(d)–(f) indicate that the microstructure changes under external magnetic field \( H \), applied along the \( x \)-axis (horizontal direction) without applied stress. In this case, the white domain grows, because the easy axis of magnetization is the \( c \)-axis of the tetragonal phase and the white domain has its easy axis along the horizontal direction, i.e. the magnetic energy stabilizes the white domain rather than the black domain; consequently, the white domain grows. Phase-field modeling is useful for predicting and analyzing the complex behavior of microstructure when we must consider both the magnetic and stress effects, simultaneously.

4.2. Modeling of microstructure changes in FePt nanogranular thin film

The FePt nanogranular microscopic formation during sputtering and the order–disorder phase transition of FePt nanoparticles in nanogranular thin film during subsequent annealing are explained in this section as an example of modeling a complex microstructure evolution by the phase-field method [61]. The FePt nanogranular structure

![Figure 1. Twin microstructure changes in Ni_{52}Mn_{48} ferromagnetic shape memory alloy under external stress and magnetic fields [55]. White and black domains have different variants depending on their tetragonal orientation.](image)
has recently become well known as a candidate for next-generation high-density recording media because of its large magnetocrystalline anisotropy. The present simulation is performed to model the following microstructure changes: the nanostructure formation in FePt nanogranular thin film during sputtering, and the subsequent phase transformation of FePt nanoparticles from the A1 to L1\textsubscript{0} structure with isothermal aging.

Figure 2 shows the two-dimensional simulation result of FePt nanogranular structure formation and the ordering of FePt nanoparticles at 923 K. Numerical values in the upper-left corner of each figure are normalized aging time. The composition of the FePt phase is assumed to be Fe-45 at%Pt. The black and white regions of droplet shape are FePt nanoparticles, and the whiteness indicates the degree of L1\textsubscript{0} ordering. Therefore, the black and white particles are the FePt(A1) disordered phase and the white one is the FePt(L1\textsubscript{0}) ordered phase, respectively. The matrix (gray part) is an amorphous alumina phase.

4.3. Phase decomposition in Co–Sm–Cu ternary rare-earth magnet

The Sm–Co rare-earth hard magnet has been investigated because of its excellent coercivity and the thermal stability of its magnetic property, which are influenced by the microstructure morphology. In this section, we focus on the phase separation between Sm(Co,Cu)\textsubscript{5} and Sm\textsubscript{2}(Co,Cu)\textsubscript{17} phases in Sm–Co–Cu ternary alloy, and demonstrate the phase-field simulation of the phase decomposition (Sm(Co,Cu)\textsubscript{5} + Sm\textsubscript{2}(Co,Cu)\textsubscript{17}) in this alloy by the phase-field method [64].

Figure 3 shows the two-dimensional simulation of isothermal phase decomposition in a Co-13 at.%Sm-5 at.%Cu rare-earth magnet at 1093 K on (1120) plane of hcp crystal structure, where vertical direction is parallel to c-axis [64]. The upper and the lower rows show the temporal microstructure changes of the Sm and the Cu composition field, respectively.
and Goll [66] that the increase of the Cu content in the Sm$_2$Co$_7$ phase decreases the magnetocrystalline anisotropy constant $K_1$, which induces a deep magnetic energy well in the interface region that acts as a pinning site and inhibits the magnetic domain boundary migration. As shown in figure 3, the phase-field simulation provides information on the local solute behavior in the interface region.

### 4.4. Microstructure design in Fe–Cr–Co spinodal magnet

Fe–Cr–Co alloy is known to be a spinodal hard magnet in practical commercial use, and an excellent magnetic property has been attained by controlling the internal microstructure through thermomagnetic treatment and step aging. The following example shows the phase-field simulation of the microstructure design of Fe–Cr–Co alloy [54].

Figure 4 shows the two-dimensional simulation of the phase decomposition of the $\alpha$-bcc phase in a Fe-35 at.%Cr-12 at.%Co spinodal magnet during magnetic aging at 963 K and subsequent step aging at 953 K and 903 K [54].

![Figure 4](image)

**Figure 4.** Two-dimensional simulation of phase decomposition of $\alpha$-bcc phase in Fe-35 at.%Cr-12 at.%Co spinodal magnet during magnetic aging at 963 K and subsequent step aging at 953 K and 903 K [54].

In the simulation of the step aging at 953 and 903 K, the magnetic energy is not considered, i.e. we assume the condition $E_{\text{mag}} = 0$ for simplicity. The middle row of figure 4 represents microstructure changes due to step aging at 953 K; the initial microstructure is the same as that in figure 4(d). When we examine the microstructure changes from figures 4(d)–(g), the Fe- and Co-rich $\alpha_1$ phase, i.e. the dark part in the figure, is further nucleated and the number of $\alpha_1$ precipitates is increased. Although the external magnetic field is turned off, we note the global morphology of the microstructure obtained retains the lamellae shape (see figure 4(g)). The bottom row of figure 4 shows microstructure changes upon the subsequent step aging at 903 K, where the microstructure in figure 4(g) is used as the initial microstructure. With aging, the Fe and Co compositions in the $\alpha_1$ phase and the Cr composition in the $\alpha_2$ phase are increased, which is clearly recognized from the change in contrast from figures 4(g)–(j). When we focus on the $\alpha_2$ phase (Cr-rich white part) in the lamellae structure, the width of the $\alpha_2$ phase is seen to decrease with aging, i.e., the volume fraction of the $\alpha_2$ phase decreases and that of the $\alpha_1$ ferromagnetic phase increases with aging. The morphological and temporal developments of the simulated microstructures are in good agreement with the experimental results that have been observed for this alloy system [67–68].

### 4.5. Microstructure change in Fe–C steel under external magnetic field

The Fe–C system is a fundamental structural material and its applications extend to every industry. There is no doubt that Fe–C steel is highly useful, but its internal microstructure changes are extremely complicated because a variety of phase transformations and precipitation phenomena are included in this system. The following simulation is an attempt at modeling this complex microstructure change by the phase-field method.

Figure 5 shows the two-dimensional simulation of phase transformation and microstructure development in Fe-0.4 mass% C at 1023 K with external magnetic field along vertical direction [69]. The microstructure change in the upper row demonstrates the temporal evolution of the phase field that represents the polycrystalline grain structure, where the gray and white regions indicate the $\alpha$ ferrite phase and $\gamma$ austenite phase, respectively. The lower row shows the temporal development of the carbon composition field.

![Figure 5](image)

**Figure 5.** Two-dimensional simulation of phase transformation and microstructure development in Fe-0.4 mass% C at 1023 K with external magnetic field along vertical direction [69]. The microstructure change in the upper row demonstrates the temporal evolution of the phase field that represents the polycrystalline grain structure, where the gray and white regions indicate the $\alpha$ ferrite phase and $\gamma$ austenite phase, respectively. The lower row shows the temporal development of the carbon composition field.
along the vertical direction [69]. The sequence of phase transformation and microstructure changes with isothermal aging is represented in figures 5(a)–(d). The numerical values in each figure are dimensionless aging time. The microstructure change in the upper row in figure 5 demonstrates the temporal evolution of the phase field that represents the polycrystalline grain microstructure. The gray and white regions indicate α-ferrite and γ-austenite phases, respectively. The lower row of figure 5 shows the temporal development of the carbon composition field. The local composition value in the microstructure is represented in grayscale, and a dark shade means a high concentration of carbon atoms, i.e., pure Fe and Fe-1 mass%C correspond to white and black, respectively.

At the initial stage of aging (figure 5(a)), carbon atoms begin to segregate in the grain boundary region of the polycrystalline α phase, and the carbon-enriched part becomes slightly elongated along the vertical direction. This tendency is enhanced with aging and the γ phase nucleates at the grain boundary region with high carbon concentration (See figure 5(b)). As shown in figures 5 (b) and (c), the γ phases grow along the vertical direction so as to follow the carbon-enriched region at the grain boundary, and the volume fraction of the γ phase increases. Finally, it is seen in figure 5(d) that the (α+γ) two-phase structure elongated along the external magnetic field. This microstructure change has been observed experimentally by Ohtsuka et al [70] and these simulation results are in good agreement with the experimental findings.

5. Summary

Phase-field methodology has both energetic and dynamic approaches. The energetic approach is a general total-energy evaluation method, where the thermodynamics in the CALPHAD method [51], Micromechanics [49, 50] and Micromagnetics [46–48] are systematically synthesized. Since energy is a scalar quantity, the energy calculation methods developed in different fields of materials science are easily combined, theoretically. On the other hand, the dynamic approach is a simulation of inhomogeneous microstructure developments using governing differential equations, wherein one can deal with the evolution of arbitrary morphologies and complex microstructures without explicitly tracking the positions of interfaces. Furthermore, enormous numbers of computer simulation techniques for solving differential equations have been developed in computational fluid dynamics and computational mechanics, which will also be useful for phase-field simulation. Since the scale of microstructure covered by the phase-field method is mostly the mesoscopic scale, the phase-field method is used as a buffer simulation between the first-principals atomistic calculation and the macroscopic computer-aided process simulation such as the finite-element method [71, 72], and the continuum phase-field model can be applied to any microstructure changes in alloys, ceramics and polymer systems. Therefore, the phase-field method will be a suitable simulation method for understanding the mesoscopic and multiscale complex microstructure formations in materials science.

However, mesoscopic microstructure formations involve highly complex nonlinear phenomena relevant to many process and material factors, and we must keep in mind that perfect precise prediction of nonlinear phenomena is often impossible in nature. Although the phase-field method has great flexibility for describing complex microstructure changes, the nonempirical quantitative prediction of the development of mesoscopic complex microstructure is impossible at this time. However, because the phase-field methodology can be used to model the complex microstructure changes quantitatively, it will be possible to search for the most desirable microstructure by using this method as a design simulation, i.e. through computer trial-and-error testing. Therefore, the most effective and practical strategy for developing advanced materials is as follows. Firstly, we elucidate the mechanism of microstructure changes experimentally, then we model the microstructure evolutions quantitatively by the phase-field method on the basis of the experimental results, and finally, we search for the most desirable microstructure while simultaneously considering both the simulation and experimental data. Furthermore, accumulating these phase-field models (each simulation program itself) as a database will provide a promising approach to establishing effective materials design. The simulations of magnetic materials demonstrated in this paper are one set of trials and represent the first uses of this concept.

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